GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[XX] ORIGINAL [ ] REVISION NO. _____

Project No. X-20-805 (T5129-0A0) GTRC/~~GIT~~ DATE 7 / 31 / 86

Project Director: ~~D. Kyser~~ Dr. T.L. Eddy School/~~XXX~~ Cont. Ed.

Sponsor: National Science Foundation

Type Agreement: Grant No. CBT-8612190

Award Period: From 6/1/86 To ~~8~~/31/87 (Performance) ~~8/31/87~~ 11/30/87 (Reports)

Sponsor Amount:	This Change	Total to Date
Estimated: $		$ 22,127
Funded: $		$ 22,127

Cost Sharing Amount: $ 1,138 Cost Sharing No: X-20-212

Title: Workshop on Thermal Plasma Systems and Engineering August 17 to 20, 1986, New Hampshire.

ADMINISTRATIVE DATA OCA Contact John B. Schonk ext. 4820

1) Sponsor Technical Contact:

E.M. Sparrow
National Science Foundation
Eng/CBT
Washington, DC 20550
202/357-9606

2) Sponsor Admin/Contractual Matters:

C.T. Henny
National Science Foundation
DGC/Eng
Washington, DC 20550
202/357-9629

Defense Priority Rating: N/A Military Security Classification: N/A

(or) Company/Industrial Proprietary: N/A

RESTRICTIONS

See Attached NSF Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

COMMENTS:

No funds may be expended after 5/31/87.

Funds are allocated as follows: X-20-805 =$22,127

E-25-811 = 6,973

Total =$29,100

COPIES TO:

SPONSOR'S I. D. NO. 03.107.000.87.001

Project Director	Procurement/GTRI Supply Services	GTRC
Research Administrative Network	Research Security Services	Library
Research Property Management	**Reports Coordinator (OCA)**	Project File
Accounting	Research Communications (2)	Other Jones

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

IN-2 SR-300

Date 12/8/87

Project No. X-20-805 School/~~ESS~~ Cont. Ed.

Includes Subproject No.(s) ~~E-25-811~~ / Eddy

Project Director(s) D. A. Kyser GTRC / ~~GTI~~

Sponsor National Science Foundation

Title Workshop on Thermal Plasma and Engineering

Effective Completion Date: 8/31/87 (Performance) 11/30/87 (Reports)

Grant/Contract Closeout Actions Remaining:

- [x] None
- [ ] Final Invoice or Final Fiscal Report
- [ ] Closing Documents
- [ ] Final Report of Inventions
- [ ] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other

Continues Project No. Continued by Project No.

COPIES TO:

Project Director
Research Administrative Network
Research Property Management
Accounting
Procurement/GTRI Supply Services
Research Security Services
Reports Coordinator (OCA)
Legal Services

Library
GTRC
Research Communications (2)
Project File
Other Duane Hutchison
Angelia DuBois
Russ Embry

FORM OCA 69.285

FINAL REPORT

WORKSHOP ON THERMAL PLASMA SYSTEMS AND ENGINEERING

By
T. L. Eddy
J. V. R. Heberlein

Under
NATIONAL SCIENCE FOUNDATION GRANT CBT 8612190

For the Period June 1, 1986 to August 31, 1987

October, 1987

GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
THE GEORGE W. WOODRUFF SCHOOL OF MECHANICAL ENGINEERING
ATLANTA, GEORGIA 30332

GTRI
GEORGIA TECH RESEARCH INSTITUTE

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address	2. NSF Program	3. NSF Award Number
Georgia Tech Research Institute Atlanta, Georgia 30332	Chemical, Bio-medical & thermal Engr.	CBT 8612190
	4. Award Period From 6-1-86 To 8-31-87	5. Cumulative Award Amount $29,100

6. Project Title

Workshop on Thermal Plasma Systems and Engineering

PART II—SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

A workshop on thermal plasma systems was held August 15-18, 1986 to determine the state of the art and research needs of industry. The workshop focused on the thermal plasma applications of plasma melting and smelting of metals; plasma spraying of metals, ceramics and other materials; and plasma synthesis of powders and chemicals. The workshop, held in Concord, NH, was attended by 12 R&D personnel from industry and national labs, as well as 21 university professors. A final report entitled "NSF Workshop on Thermal Plasma Systems" is available from NSF. The general research needs were found to be: 1) the development of techniques to measure concentrations, temperatures, and reaction or heating rates for gas species and particulates in complex or dirty industrial environments; 2) the development of models which are less idealized and more related to industrial processing for design and process control; 3) specific research into process mechanisms which are not well understood; and 4) scientific measurements or calculations of relevant thermodynamic, transport and radiative properties (e.g., collision cross sections or transition probabilities) to reduce the uncertainty in experimental results and theoretical predictions. Specific recommendations are made in the final report.

PART III—TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	X				
b. Publication Citations		X			
c. Data on Scientific Collaborators	X				
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other *(specify)* Bound copies of Workshop Proceedings			X		

2. Principal Investigator/Project Director Name *(Typed)*	3. Principal Investigator/Project Director Signature	4. Date
T. L. Eddy		12-2-87
J.V.R. Heberlein		9-25-87

PART IV - SUMMARY DATA ON PROJECT PERSONNEL

NSF Division CBT

The data requested below will be used to develop a statistical profile on the personnel supported through NSF grants. The information on this part is solicited under the authority of the National Science Foundation Act of 1950, as amended. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. NSF requires that a single copy of this part be submitted with each Final Project Report (NSF Form 98A); however, submission of the requested information is not mandatory and is not a precondition of future awards. If you do not wish to submit this information, please check this box ☐

Please enter the numbers of individuals supported under this NSF grant.
Do not enter information for individuals working less than 40 hours in any calendar year.

*U.S. Citizens/ Permanent Visa	PI's/PD's		Post-doctorals		Graduate Students		Under-graduates		Precollege Teachers		Others	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
American Indian or Alaskan Native												
Asian or Pacific Islander												
Black, Not of Hispanic Origin												
Hispanic												
White, Not of Hispanic Origin	2											1
Total U.S. Citizens	2											1
Non U.S. Citizens												
Total U.S. & Non-U.S. ..												
Number of individuals who have a handicap that limits a major life activity.												

*Use the category that best describes person's ethnic/racial status. (If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)

AMERICAN INDIAN OR ALASKAN NATIVE: A person having origins in any of the original peoples of North America, and who maintains cultural identification through tribal affiliation or community recognition.

ASIAN OR PACIFIC ISLANDER: A person having origins in any of the original peoples of the Far East, Southeast Asia, the Indian subcontinent, or the Pacific Islands. This area includes, for example, China, India, Japan, Korea, the Philippine Islands and Samoa.

BLACK, NOT OF HISPANIC ORIGIN: A person having origins in any of the black racial groups of Africa.

HISPANIC: A person of Mexican, Puerto Rican, Cuban, Central or South American or other Spanish culture or origin, regardless of race.

WHITE, NOT OF HISPANIC ORIGIN: A person having origins in any of the original peoples of Europe, North Africa or the Middle East.

THIS PART WILL BE PHYSICALLY SEPARATED FROM THE FINAL PROJECT REPORT AND USED AS A COMPUTER SOURCE DOCUMENT. DO NOT DUPLICATE IT ON THE REVERSE OF ANY OTHER PART OF THE FINAL REPORT.

Georgia Tech

THE GEORGE W. WOODRUFF SCHOOL OF
MECHANICAL ENGINEERING

Georgia Institute of Technology
Atlanta, Georgia 30332-0405

October 9, 1987

Dr. Robert Goulard
Thermal Systems and Engineering
National Science Foundation
1800 G Street, NW
Washington, D.C. 20050

Dear Dr. Goulard:

Please find enclosed two copies of our final report for NSF Grant No. CBT 8612190, entitled "Workshop on Thermal Plasma Systems and Engineering" and associated forms.

Also enclosed is an 8.5x11" reproducible copy of the bound and distributed proceedings of the workshop (of which you have previously received 56 copies).

The distribution of the Workshop Proceedings to date follows:

	Copies
National Science Foundation	56
Participants (including NSF personnel and some who were not able to attend)	37
General Distribution to plasma-related universities and departments of universities	77
Individual requests to date	25
Remaining copies	55
	250

We have received a number of compliments on the workshop report, both as to its content and form. We hope that it is useful to NSF in the promotion of necessary research in the thermal plasma area.

Sincerely

Thomas L. Eddy
Associate Professor

PUBLICATION CITATION

for

NSF Grant: CBT 8612190

Title: "Workshop on Thermal Plasma Systems and Engineering"

Principal Investigators: T. L. Eddy and
J.V.R. Heberlein

Citation:

1. T. L. Eddy and J.V.R. Heberlein,
"NSF Workshop on Thermal Plasma Systems",
Published Final Report NSF Grant CBT 8612190,
Georgia Institute of Technology, Atlanta, May, 1987.

NSF WORKSHOP

ON

THERMAL PLASMA SYSTEMS

August 15-18, 1986

New Hampshire Highway Hotel

Concord, New Hampshire

Edited by

T. L. Eddy, Georgia Institute of Technology

J.V.R. Heberlein, Westinghouse Research and Development Center

Jointly Sponsored by

National Science Foundation

Georgia Institute of Technology

Westinghouse Research and Development Center

May, 1987

FOREWORD

This workshop was funded in part by the National Science Foundation under Grant No. CBT-8612190. We acknowledge the input and encouragement of Dr. R. Rostenbach, Dr. W. Aung, Dr. E. Sparrow and Dr. M. Lih during the planning stages of the workshop, to Dr. N. Suh for his contribution during the workshops, and to Dr. R. Goulard for his participation at the workshop and his continued interest and suggestions to improve the quality of these proceedings. Above all, we want to thank the many contributors for their extraordinary efforts in making this workshop a success. We also thank R. Eschenbach and W. Roman, who were unable to attend, for their contributions during the planning of the industrial sessions and the summarizing phase of the workshop. The assistance of Karen Burkhart, Kaye Fuller, Barbara Gregory and Patricia Thomas in the excellent preparation of the manuscript is also appreciated.

The opinions, findings, and recommendations expressed in this publication are those of the Workshop contributors or editors and do not necessarily represent the views of the National Science Foundation, other sponsoring organizations, or of the organizations which the contributors represent.

Cover: Simplified conventional, direct reduction-electric furnace, and plasma steelmaking (modified with permission from D.R. MacRae, AIChE Symposium Series, No. 186, Vol. 75, pp. 25-30, 1979).

PREFACE

The National Science Foundation sponsors workshops in many fields of science and engineering as a means of extracting the best collective wisdom of the community on a subject. This workshop on Thermal Plasma Systems was designed to identify the problem areas and knowledge gaps that exist in expanding intellectual frontiers of the field and advancing technology through major innovations.

The objective is consistent with the original mandate of the Foundation: to promote and advance scientific progress in the United States, to provide health, prosperity and welfare to its people, and to secure national defense. That mandate includes a role as a catalyst in changing the culture of universities, the research community, and industry, whenever such a role is warranted.

In carrying out that mandate the main agenda for the ENGINEERING Directorate of NSF is:

- To enhance the Nation's economic competitiveness.
- To improve the quality of life for our citizens.
- To capture new scientific, technological, and intellectual opportunities for the year 2000.
- To contribute to national security.

Some of the ways this is being done is by placing emphasis on strengthening the current engineering science base; establishing a science base in technology driven fields, such as design and manufacturing; developing the academic infrastructure in emerging technology areas, such as biotechnology and lightwave technology; and bringing about innovation of new technologies in all engineering fields, but especially in critical technologies and cross-disciplinary research.

The ENGINEERING Directorate is also embarking on programs designed to strengthen undergraduate education, since in engineering a majority of the practitioners who largely determine the quality of our products -- and thus our competitivesness -- hold only a baccalaurate degree.

This agenda is important because it addresses a fundamental problem facing our nation today: the erosion of the U.S. industrial base. Over the short-term a number of actions -- technological and nontechnological -- must be taken to increase the quality of our products. In the long-term, however, we must rely on advances in technological innovation to carry the day. Much of the U.S. productivity increase since the 1930's has been due to such innovation. Only through the production of high-value added goods, in both mature as well as high technology industries alike, can the U.S. hope to maintain its standard of living. One key in all of this is that we have to be innovative and meticulous in design and manufacturing.

The challenge to the research community is to generate both the knowledge, which can take us beyond the limits of even our current imagination, and the human resources, who can improve the lot of their fellow citizens and the well-being of the Nation.

Investment in research has borne multiple benefits in the past. This generation cannot become an exception to the rule. The challenge of this research community on thermal plasma systems is to provide the intellectual leadership by identifying the opportunities that transcend a more linear extrapolation of current thought.

On behalf of the National Science Foundation, I would like to express our indebtedness to those who made this workshop possible.

Nam P. Suh
Assistant Director
for Engineering

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

THERMAL PLASMA SYSTEMS

CHAPTER 1

INTRODUCTION

J.V.R. Heberlein
Westinghouse R & D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

T. L. Eddy
Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

1. INTRODUCTION

The purpose of the workshop on Thermal Plasma Systems and Engineering is to provide the National Science Foundation and others with the following information.

(1) What are the important thermal plasma processes which are in present use and which will be used in the near future in the industrial and commercial sectors.

(2) What specific research information needs to be determined for the important thermal plasma processes to significantly advance the state of the art.

(3) What priorities for research might be established for funding support by the Thermal Systems and Engineering Program of the National Science Foundation to enhance development in thermal plasma systems and engineering.

The emphasis in this report is on thermal plasma processing. Most thermal plasma processing involves materials on which research funding for the extraction, development, or forming is under the auspices of other programs of NSF, or elsewhere. In this report, the recommended research priorities are focused on the area of thermal research instead of materials research --- plasma-related thermodynamics, heat transfer, fluid flow and chemical reactions rather than solid/liquid/molten processes with combustion/catalyst/coke reactions and emphasis on product structure, mechanical and other "metallurgical" properties of the product. Research papers emphasizing plasma metallurgy have been mainly devoted to investigating what goes in and what comes out of the black box called the plasma reactor. Thermal plasma research papers are mainly devoted to investigating what happens within the black box. The roles complement each other. Both are necessary to improve the overall quality and economics of the final product.

The workshop participants included 12 speakers from industry and National Labs, and 14 speakers from universities and seven observers with backgrounds in related areas. The list of attendees is given in Table II. The industrial people have a plasma background, but have a product to sell. They realize the importance of understanding the thermal plasma process sufficiently well enough to control the quality and cost of the saleable product. Their contributions focused on the thermal processing aspects rather than the metallurgical analysis at this workshop. The university people are active in the broad spectrum of plasma, plasma-particulate and plasma-surface research under equilibrium and nonequilibrium conditions. As a group, they are familiar with essentially all aspects related to thermal plasmas including diagnostics, modeling systems or processes, and determining thermodynamic and transport properties. Their forte, as a group, is in thermal plasma science rather than material plasma science, though several are experts in the latter as well. Seven of the 26 invited speakers and session chairmen are from other countries. This indicates the importance of thermal plasma processing on an international level and the need for the United States to be able to be commercially competitive in this area.

The final workshop program is given in Table I. The first session Friday evening included talks by Dr. Nam P. Suh, Associate Director for Engineering, NSF, and Professor E. Pfender. Presentations of the state of the art and needs in

plasma system applications by industry representatives composed the first half-day working session, Saturday morning. This was followed by three half-day sessions on technical areas, presented predominantly by university professors. Interspersed with the technical area presentations were 6-8 person group discussions and determinations of priorities in a given technical area, culminating in a total group meeting to summarize recommendations. The initial plan required only session chairmen, and group leaders to attend the summary meetings; however, we found that essentially all participants attended and contributed to the summary meetings. As a result, the final session on Monday morning was modified to exclude the summary of recommendations, but did include a presentation on inferences from recent plasma technology studies by Dr. J.V.R. Heberlein, and a discussion of the "Hot" club of France (a plasma related industry-university consortium) led by Professor P. Fauchais.

We present in the following an Executive Summary, first of the selected plasma processing applications, then of the research needs in the scientific areas, and finally of conclusions on research priorities with regard to impact on the selected technologies, together with recommendations for further actions to achieve the envisioned impact. The sections following the executive summary contain the individual summaries of the workshop presentations, grouped as they were presented in different sessions.

TABLE I. FINAL WORKSHOP PROGRAM

NSF WORKSHOP ON THERMAL PLASMA SYSTEMS AND ENGINEERING
New Hampshire Highway Hotel, Concord, N.H.
August 15-18, 1986

Friday Evening, August 15, 1986

6:00-7:00	Registration and Social Hour (cash bar)
7:00-8:00	**Dinner**
8:00-9:00	Welcome: Dr. Robert Goulard, NSF Purpose of Workshop: Dr. J.V.R. Heberlein Organization of Workshop: Professor T.L. Eddy Keynote Address: Dr. Nam P. Suh Associate Director for Engineering, NSF
9:00-9:15	Break
9:15-10:15	Technical Introduction: What is special about plasmas?: Professor E. Pfender

Saturday, August 16, 1986

7:30-8:00	**Continental Breakfast**
	Plasma System Applications - State of the Art and Research Needs
8:00-9:00	Metal Melting
9:00-10:00	Plasma Spraying
10:00-10:15	Break
10:15-11:15	Powder Synthesis
11:15-12:15	Chemical Processing and Smelting
12:30-1:30	**Lunch**
	Technical Areas Related to Plasma Systems - State of Art
2:30-3:15	Diagnostics Review
3:15-4:30	Diagnostics Discussion
3:15-6:00	Break materials available in the Webster Room
4:30-5:15	Thermophysical Properties Review
5:15-6:00	Thermophysical Properties Discussion
6:30-7:30	**Dinner**
8:00-9:00	Session chairmen and subgroup leader meeting for previous session (others may attend)

TABLE I. (continued)

Sunday, August 17, 1986

7:30-8:00	**Continental Breakfast**
8:00-8:45 8:45-9:30 9:30-10:00	Review of Equilibrium and Nonequilibrium Modeling and Scaling
10:00-11:30	Break materials available in Webster Room
10:00-12:30	Discussion (with various subgroups focussing on each of the above)
12:30-1:30	**Lunch**
1:30-2:30	Session chairmen and subgroup leaders meeting (others may attend)
3:30-4:00	Review of Plasma-Solid Boundary Layers, Sheaths
4:00-5:30	Break materials available in Webster room
4:30-6:00	Discussion
6:00-7:00	**Dinner**
7:30-8:15	Review of Plasma-Particle Interactions
8:15-8:45	Review of Nucleation and Particle Growth
8:30-10:00	Break materials available
8:45-10:00	Discussion
10:00-10:45	Session chairmen and subgroup leaders meeting (others may attend)

Monday Morning, August 18, 1986

7:30-8:00	**Continental Breakfast**
Concluding	Statements and Discussions for Future Research
8:00-8:30	Inferences Drawn from Recent Studies on the Role of Plasma Technology: J.V.R. Heberlein
8:30-9:00	Diagnostics
9:00-9:20	Thermophysical Properties
9:20-10:00	Modeling and Scaling
10:00-10:15	Break
10:15-11:00	Plasma-Solid and Heterogeneous Interactions
11:00-11:45	Plasma-Particle and Nucleation/Particle Growth
11:45-12:45	**Lunch**

TABLE II. ATTENDEES

NSF WORKSHOP ON THERMAL PLASMA SYSTEMS AND ENGINEERING
New Hampshire Highway Hotel, Concord, N.H.
August 15-18, 1986

1. Professor Harold M. Anderson
Department of Chemical and Nuclear Engineering
University of New Mexico
Albuquerque, NM 87131
(505)277-5661

2. Dr. N. Barcza
Council for Mineral Technology
200 Hans Strijdam Road
Private Bag X3015
Randburg
2125 South Africa

3. Professor David M. Benenson
Department of Electrical and Computer Engineering
207 Bell Hall
State University of New York at Buffalo
Buffalo, NY 14260
(716)636-2422

4. Professor Maher Boulos
Chemical Engineering Department
Faculty of Applied Sciences
Universite de Sherbrooke
Sherbrooke, Quebec
Canada J1K2R
(819)821-7168

5. Dr. H. Casey
MS G770
Los Alamos National Laboratory
P. O. Box 1663
Los Alamos, NM 87545
(505)667-4366

6. Professor John Conrad
Department of Nuclear Engineering
University of Wisconsin - Madison
Madison, WI 53706
(608)263-1609

7. Professor Clifford J. Cremers
Mechanical Engineering Department
University of Kentucky
Lexington, KY 40506
(606)257-3585

8. Professor Thomas L. Eddy
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0405
(404)894-3210

9. Professor John F. Elliot
Room 4-140
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139
(617)253-3305

10. Professor P. Fauchais
Laboratory Thermodynamique
Universite de Limoges
123 Avenue Albert Thomas
87060 Limoges Cedex, France
011-33-(55)-79.46.22

11. Dr. Jerome Feinman
J. Feinman and Associates
2654 Sperber Lane
Grand Junction, CO 81506
(303)243-5533

12. Professor Steven Girshick
Mechanical Engineering Department
University of Minnesota
Minneapolis, MN 55355
(612)625-0099

13. Dr. Robert Goulard
Thermal Systems and Engineering
Room 1126
National Science Foundation
1800 G Street Northwest
Washington, D.C. 20050
(202)357-9606

14. Mr. D. Harris
APS Materials
153 Walbrook
Dayton, OH 45405
(513)278-6547

15. Dr. J.V.R. Heberlein
Building 302, Room 209
Westinghouse R & D Center
1310 Beulah Road
Pittsburgh, PA 15235
(412)256-1581

16. Professor Rolf Hernberg
Mechanical Engineering Department
Stanford University
Stanford, CA 94305
(415)723-1745

17. Dr. C. B. Holden
257 Church Street
Doylestown, OH 44230
(216)658-2793

18. Dr. David Houck
GTE Materials
Hawes Str.
Towanda, PA 18848
(717)265-2121

19. Professor J. Kunc
Depts. of Aerospace Engineering and Physics
GER-240
University of Southern California
Los Angeles, CA 90089-0192
(213)743-7992

20. Professor Alan Larson
School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0405
(404)894-3266

21. Mr. Richard Liebermann
Sylvania Lighting
HID Department
100 Endicott Street
Danvers, MA 01923
(617)777-1900

22. Dr. D. Mac Rae
Bethlehem Steel Corporation
Research Center
Bethlehem, PA 18016
(215)694-6956

23. Dr. Michael E. McIlwain
Idaho National Engineering Lab
EG&G Idaho, Inc.
ILF-232
P. O. Box 1625
Idaho Falls, Idaho 83415
(208)526-8130

24. Dr. T. N. Meyer
ALCOA Technical Center
Alcoa Center, PA 15069
(412)337-2580 or 339-6651

25. Professor David B. Miller
Department of Electrical Engineering
Mississippi State University
Mississippi State, MS 39762
(601)325-3648

26. Professor R. J. Munz
Department of Chemical Engineering
McGill University
3480 University Street
Montreal, PQ
CANADA H3A 2A7
(514)392-5432

27. Dr. Dieter Neuschütz
Friedr. Krupp GmbH
Kruppforschungsinstitut
Munchener Strasse 100,
D4300 Essen 1, West Germany
011-49-(201)-188-2842

28. Professor E. Pfender
Mechanical Engineering Department
University of Minnesota
Minneapolis, MN 55355
(612)625-6012

29. Professor Sidney A. Self
Mechanical Engineering Department
Stanford University
Stanford, CA 94305
(415)723-1745

30. Dr. Nam P. Suh
Assistant Director for
Engineering
National Science Foundation
1800 G Street Northwest
Washington, D.C. 20050
(202) 357-9832

31. Professor M. Venugopalan
Department of Chemistry
Western Illinois University
Macomb, IL 61455
(309)298-1538

32. Dr. Gerald J. Vogt
Material Science and Technology
Division
MS C348
Los Alamos National Laboratory
P. O. Box 1663
Los Alamos, New Mexico 87545
(505)667-5813

33. Professor Toyonobu Yoshida
Department of Metallurgy and
Materials Science
University of Tokyo
Bunkyo, Tokyo 7-3-1 Hongo 113
Japan
03-812-2111 (X7100)

THERMAL PLASMA SYSTEMS

CHAPTER 2

EXECUTIVE SUMMARY

J.V.R. Heberlein
Westinghouse R & D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

T. L. Eddy
Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

2.1 INTRODUCTION

The problems that face American manufacturing industry are very widely discussed. The increasingly negative balance of payment continues to be a testimony of some of these problems. To increase manufacturing competitiveness, the latest scientific and technological advances must be utilized. This is particularly important with respect to technologies which are still in early growth stages. Thermal plasma processing represents one of these technologies where the scientific advances in the past two decades have increased our basic understanding and have made it possible to increase the chance of success when the technology is transferred to an industrial process.

Thermal plasmas have been used for processing of materials and chemicals since the last century. However the development of plasma technology was commercially successful only in a few cases. Only when electricity became abundant and when plasma technology saw unprecedented advances in the context of worldwide efforts to harness fusion technology and in the context of the U.S. space program, did we see a spreading of this technology into different areas of manufacturing. The advances of plasma technology have encountered resistance because (a) economically, the advantages of using plasmas must outweigh the cost of using electricity, a fact which sets a certain lower limit to the value added to the product in the plasma process, (b) the use of plasmas multiplies the number of parameters controlling the process, making process optimization a more complicated task, and (c) intuition developed through the use of other technologies cannot necessarily be transferred to plasma processes, requiring specific education in this area. An example for the last item is that enhanced cooling of an electric arc plasma generally results in increased peak temperatures.

Because of these reasons there have been numerous studies and several workshops about the potential of thermal plasma technology discussing the pros and cons for a variety of applications, and the required advances for making the plasma utilization successful. Also, the present workshop has had the objective of determining the specific technological problems, the solutions of which would have the most significant impact on advancing the technology in some selected applications. A second objective has been to familiarize scientists who appeared to have the scientific tools for some of the specific problems with these problems in the applications of plasma technology to materials processing and manufacturing.

Our approach to achieving these objectives was to first present overviews of the technology status in selected applications. This was followed by presentations on the state of the art in those scientific areas which are closely related to the plasma technology in the considered applications. Discussion sessions in smaller groups were held to establish how the available scientific tools could be used for advancing the plasma application, and what research in the scientific areas would be needed to achieve such advances.

While the presentations in general conveyed a good image of the technologies and of the state of the art in the scientific areas, the discussion sessions did not always lead to a consensus, and some conclusions were inconsistent. In particular, how far academic research should attempt (or would be able) to address the reality of industrial problems appeared occasionally as a point of contention.

In our summary of the workshop, we did not attempt to remove the diversity of the points of view presented at the workshop. However, in the conclusions we tried to present a consistent picture, which meant that occasionally choices had to be made between diverging views of certain priorities. But this report was circulated among all workshop participants in the U.S., and each participant had the opportunity to ask for an additional section containing different points of view.

2.2 SUMMARY OF SELECTED PLASMA APPLICATIONS

2.2.1 Importance of Areas

Over the past ten years, thermal plasma processing has seen a considerable growth in industrial applications as well as in scientific activity. The phenomenal growth of the plasma spray industry and the inroads being made by plasma processes in the steel industry are testimony of the former. The growth of the scientific conferences devoted to plasma processing (e.g. the International Symposium on Plasma Chemistry) and the establishment of specialized sessions in more general society meetings (e.g. MRS Symposium, IEEE Plasma Science Conference) prove the latter. This growth has been stimulated in part by advances in our understanding of plasma (technology push), and in part by the need of the industry for improved manufacturing methods (applications pull). For this workshop, the discussion has been limited to those industrial applications, in which

(a) a growth of thermal plasma technology is foreseen, and
(b) where technical and scientific advances would have a significant impact on the industrial production technology.

We, therefore, neglected such established applications as welding and cutting of metals, and lighting through discharge lamps.

2.2.2 General Advantages of Thermal Plasma Processes

The three primary characteristics of thermal plasmas result in certain advantages for processing applications.

(1) The high energy density of the plasma in the reactor allows increased production in a smaller installation with associated capital cost savings.

(2) Use of electrical energy for heating decouples the energy input from the oxygen potential of the reactants, i.e. process control is improved by separately controlling the reactant temperature and composition. Use of less expensive feed stock, and improved product quality and process efficiency are the consequences.

(3) The high temperature reaction zone leads to fast reaction rates, (i.e. chemical reactions, or melting of particles) and high quench rates. The consequences are again a wider choice of feedstock, and the possibility of making new products, such as metastable high temperature phases of compound materials.

The specific driving forces for using plasma processes in a particular industrial application are derived from these advantages.

2.2.3 Discussion of Specific Applications

Table I summarizes the issues for several applications. The column under the "need" describes the driving force behind the efforts in introducing new or alternative processes. The next column lists the specific advantages of the plasma process for the particular application. The technology issues are the areas where technological advances are required to assure success of the plasma process in this application area, and the last column lists the specific research needs which are associated with these technological advances.

2.2.3.1 Metallurgical Industry

In almost all applications in this industry, there is a need for improved productivity, more economical operation, and for improvement in the product quality. Plasma processes have the potential of answering these needs in several metallurgical applications. In particular, plasma installations offer the potential of lower capital cost and lower operating cost because of smaller size installations and the utilization of cheaper feedstock. The additional advantages over conventional technology are the improved process control and the reduced environmental impact.

The steel industry offers the largest opportunities for new plasma installations. Presently, about 25% of all steel is produced by conventional arc furnaces, and these installations are prime targets to be replaced by modern open bath plasma furnaces using nonconsumable electrodes and arc transfer to the melt (see Section 3.1). An even larger potential market is represented by the blast furnace application where plasma heating of the air reduces the amount of coke needed and allows an increase of the ore charge and, therefore, the productivity. However, with the present state of technology, utilization of plasma torches for blast furnace air preheating will remain limited to areas with a favorable electricity cost to coke cost ratio. If the preheating can be combined with reducing gas formation using powdered coal, the coke savings and productivity enhancements obtained as a consequence of plasma processes can be significant (see Section 3.3). Similarly, plasma smelting and ferroalloy production in open bath plasma furnaces depend on the technological advances to succeed on a global scale. Success of the commercialization of the plasma process will lead to less expensive, high-grade ferroalloys, or even new alloys (see Section 3.2).

Practically all of the advantages of the plasma processes are being realized in the plasma-fired cupola where untreated borings and other fine wastes are being heated and melted by the plasma gas. The processing steps of chip cleaning and compaction are eliminated, and economical recovery of waste materials is the consequence. Waste treatment of furnace dust is a similar application where the plasma process allows recovery of valuable materials and solves the problem of disposal of toxic wastes. In all of these applications, there are either some commercial plants operating or a successful pilot plant operation is being developed to full commercialization. However, full realization of the advantages of the plasma processes requires equipment related work such as scaling of the equipment (e.g. plasma torches from ~ 6MW power rating to ~ 25MW rating), improved equipment operating reliability and reduced frequency of service (e.g. longer electrode life), and process related work such as process optimization and improved control. The equipment related work requires a better understanding of electrode erosion phenomena and plasma heat transfer. The process related improvements need diagnostics on practical systems to provide the data leading to an understanding of the process details.

Table I - Summary of Selected Plasma Applications

	Application	Need	Specific Plasma Process Advantage	Status	Technology Issues	Research Need
(1)	Metallurgical Industry • Metal melting	improved product quality, improved productivity	better process control, lower operating cost, less environmental impact	commercial, expanding (Germany, Austria others)	Scaling to economical size: larger plasma torches, improved operating reliability	electrode erosion, arc control, plasma process chemistry
	• Smelting/ferro-alloy production	same	same as above; lower capital cost, inexpensive feedstock	pilot plant, limited commercial (S. Africa, Sweden)	increased thermal efficiency, improved operating reliability	plasma heat transfer, plasma process chemistry arc control
	• plasma fired cupola for chip melting	improved productivity	lower operating cost, (no feedstock pre-treatment)	pilot plant (USA)	electrode life process control	electrode erosion, process chemistry
	• blast furnace air preheating	improved productivity	lower coke consumption, increased ore charge	limited commercial (France)	electrode life, use of coal powder	electrode erosion, power injection into plasma
	• waste treatment	environmental concerns	no pretreatment of feedstock	commercial (Sweden)	process optimization	plasma process chemistry
(2)	Plasma spraying	expensive coatings on inexpensive substrate/ materials savings	high temperature allows use of high melting point materials for coatings	commercial, expanding	higher throughput increased liability, new coatings, near net shape manufacturing	plasma uniformity particle trajectory prediction
(3)	Synthesis of ceramic or metal alloy powders	inexpensive production of hi-tech ceramics, alloys	high temperature zone, quench rate allows wide selection of reactants, control of production phases	some commercial growth anticipated	product yield, control of particle size and size distribution; product phase purity	plasma reaction kinetics, nucleation and particle growth
(4)	Chemical processing	new or more economical processes	high energy density smaller installations; independent control of heat and reactants	some commercial	improved product yield;	reactant/plasma interaction, reaction kinetics,

2.2.3.2 Plasma Spraying

This plasma application is unique insofar as there is practically no competitive process for a large portion of the coating market. Plasma spraying was in 1983 an estimated $500 M/year industry with the major customer being the aerospace industry. Growth of the industry is certain if the present advances of the plasma spray technology in the automotive industry (e.g. cylinder wall coatings) and the medical industry continue. Plasma spraying relies on the high plasma temperature to melt particles of the spray material in a short time, and on the high energy density of the plasma to achieve a practical particle throughput. Coating of a substrate with an expensive superalloy or a high-temperature ceramic allows 80 to 90% materials savings compared to bulk machining. Worldwide research and development efforts are addressing the issues that would result in further expansion of the plasma spray technology, namely increased throughput and process reliability/yield. New coatings, e.g. by in-flight alloying of the spray particles and near net-shape manufacturing, are plasma spray applications in the development stage. The required research for aiding these goals is a better understanding and control of the plasma particle interaction, so that almost all of the particles arriving at the substrate are in the desired phase.

2.2.3.3 Plasma synthesis of advanced ceramic or metal alloy powders

The ceramic industry is a rapidly growing industry, with the growth anticipated to accelerate. In 1980, the world market for advanced ceramics was $4.2B, and in 1984, the Japanese market alone amounted to $2.7 billion. Plasma technology has the potential of assisting this growth by providing relatively inexpensive production processes for high purity ceramic powders. The high reaction-zone temperatures allow rapid vapor phase reactions even of refractories with a high vaporization point, and the high quench rates result in uniform particle size and in the possibility to obtain metastable high-temperature phases, such as β-WC or $\gamma \rightarrow \delta$-NbN. Plasma production of these ceramic powders has seen limited commercial application. The major issues that have to be addressed are (1) improved product yield, both by improved product collection techniques (in general) and improved predictability of the product or product phase, (2) control of particle size and size distribution, and (3) control of the agglomeration behavior of the particles. The required research ranges from the initial plasma reaction kinetics to the nucleation and particle growth processes.

2.2.3.4 Chemical Processing

There are a variety of plasma processes for chemical applications in various stages of development. Nitrogen fixation in an arc discharge is one of the oldest commercial bulk chemical plasma processes (Norway, 1905), but it turned out to be uneconomical compared to other processes a few years after it was established. Research efforts are attempting to increase the nitric oxide yield per unit of electrical energy to reduce cost. The advantages of the plasma process, namely simpler and smaller installations because of fewer processing steps and higher energy density in the reaction zone must offset the relatively high cost of electrical energy for the process to be competitive. Acetylene production is a commercial process at Huels, Germany since 1939, and research and development efforts are underway to improve the product yield and to obtain high yields with cheaper feedstocks, such as heavy oils and powdered coal instead of natural gas. After considerable development efforts in the United States, this process has been judged not economical here compared to the manufacture of ethylene (see section 6.1). Gasification of carbonaceous feedstocks by reaction with air or steam, and reforming of light hydrocarbons with steam are processes the economics of which depend strongly on the local electricity cost and local product demand and price. Drying using superheated steam appears to be an interesting application which is

being developed in Canada. Smaller installations because of the higher energy density, and better control because of the use of steam rather than combustion products are the major driving forces.

An application where all the advantages of the plasma are used is toxic waste pyrolysis in relatively small, mobile plasma units. The high temperature leads to dissociation of the toxic materials, and quenching prevents reformation. The process is commercial, and it is expected that this market will experience a considerable growth.

Most of the chemical applications need very high process yields to be economical. The knowledge about the specific reactions taking place and about the associated reaction rates has to be improved for process optimization. Reaction-zone diagnostics and reaction-kinetics modeling are required for this end.

2.3 SUMMARY OF RESEARCH NEEDS

This section summarizes and prioritizes the broad spectrum of research needs in thermal plasma processing. Major conclusions and recommendations are presented in the following section.

The most important applied research needs are in the development of models for the design of equipment and processes, in the calculation or measurement of accurate properties for model calculations or diagnostic analysis, and in developing the diagnostic methods for system control or model validation. Basic research is also needed to investigate the dominant mechanisms in plasma-surface and plasma-particulate interactions, as well as particulate nucleation and growth. The relative priority of model development, property calculation procedures or measurement, and experimental diagnostics depend upon the needs in a particular application. The major commercial applications for thermal plasmas today are:

1. Plasma melting and smelting of metals.
2. Plasma spraying of specialized coatings.
3. Plasma synthesis of powders and chemicals.

The following research needs are therefore categorized in the melt/smelt, spray, and synthesis applications under the area topics of diagnostics, properties, models, and specific research topics as follows below.

2.3.1 Diagnostics

Table II indicates the diagnostic techniques that need to be developed or perfected in the three application areas. It is important to distinguish between diagnostic techniques applied to industrial systems for process control and diagnostic techniques applied to laboratory experiments to validate or develop models for design purposes. In this section on diagnostics, the emphasis is on techniques for industrial process control or for laboratory experiments to identify dominant mechanisms or develop a data base for modelers. In the modeling section the experimental emphasis is on model verification. In Table II, as well as in Tables III and IV, the priorities are given by the numbers in the columns under the application category, with a "1" indicating first priority. Diagnostic needs with equivalent priorities are given the same number. The items are numbered (on the left) in order based on an "averaged", qualitative priority

Table II. Diagnostics Priorities for Various Applications
(Priorities decrease with increasing number.)

Need	Melt/Smelt	Spray	Synthesis
1. Gas composition:			
Arc, ambient, arc/melt interface	1		
Arc, ambient and jet		4	1
2. Gas temperature:			
Arc, ambient, arc/melt interface	1		
Arc, ambient and jet		3	3
3. Heat/mass transfer:			
To melt surface	2		
To particles(n_p,or Γ_p,V_p,T_p,d_p)		1	4
4. In-situ techniques for t_{coat},T_{coat}		2	
5. Gas velocity(flow visualization):			
Arc, ambient, arc/melt interface	5		
Arc, ambient and jet		3	2
6. Feedstock particle trajectory (flow visualization)	3	3	?
7. Velocity V_ℓ and temperature T_ℓ in melt	4		
8. In-situ techniques for ρ_{coat}, C_{coat}		5	

assuming equal weighting among the three applications (where priorities exist). Note that there are diagnostic techniques available to measure many of the parameters of Table II in an idealized environment, but not necessarily in industrial type environments. The priorities also indicate the importance of the type of measurements that need to be made to properly monitor and/or control the process.

The overall priorities indicate the following general needs in diagnostics:

1. Common to all three areas:
   a. Gas composition, C_g
   b. Gas temperature, T_g
   c. Gas velocity (flow visualization), V_g
   d. Particulate density n_p, velocity V_p, temperature T_p, and diameter d_p and size distribution.

2. Special to melting/smelting systems:
   a. At the plasma-melt interaction: gas velocity V_g, surface temperature T_s, gas and melt compositions
   b. In the melt: liquid velocity V_ℓ and temperature T_ℓ as a function of space and time.

3. Special to spray coating:
   a. In situ measurements for the coating thickness, t_{coat}, temperature T_{coat}, density ρ_{coat}, and composition C_{coat}.

Other desired diagnostic methods included real-time powder stoichiometry, total enthalpy probes, insertable fibre-optic probes (for local radiation measurements), and improved methods to determine the gas and electron temperature.

2.3.2 Modeling Systems

Table III indicates the priority of needs assessed in the modeling area. The models obtained should allow one to model the phenomena within the context of an industrial system. The models may be empirical, semi-empirical or analytical, but need to consider the complex set of species, reactions, flows, transport, etc. that can occur in practice. Industry is not interested in idealized models to describe laboratory experiments.

Note that the order of priorities differs considerably between the set designated as "industrial priorities" and that designated "university priorities". The industrial priorities are from the integrated results of the four discussion subgroups and appear to represent the view of all the attendees with deference to the industrial needs. The university priorities are from the modeling session chairman and appear to represent what is needed to understand what is happening so that the process can be modeled. The difference may reflect the difference in focus, rather than absolute importance. Priorities also differ somewhat between industrial categories, depending on the processes involved.

In addition to the items in Table III, models for furnace/reactor design, overall process optimization, control, equipment safety and economic analysis are desired by industry. In fact, the capability of making a good heat balance on a reactor is critical to economical operation and often the initial decision to install such a reactor/furnace.

Models of industrial processes should consider the fact that reactant mixing is a key part of many chemical synthesis routes and control of mixing is thought to have a major influence upon the product; hence, models should include mixing features of the reactor. Models of industrial processes should also include/allow for the generation of metallic fumes (submicron) of various types, including alloys and generation of ceramic powders (e.g., SiC, TiB_2, AlN, B_4C, BN, as well as oxides such as Al_2O_3, ZrO_2 and Y_2O_3) with appropriate materials. Modeling the reactive processes should be done in the presence of hydrogen which is more appropriate than argon in many processes. Reactive processes (and hence reaction rates) of interest should be sure to include the chlorides (e.g., $SiCl_4$, $TiCl_4$, $AlCl_3$, etc.), hydrocarbons, chlorocarbons, ammonia and many others. For additional processes of interest, consult survey articles on the production of certain materials.

2.3.3 Thermophysical Properties

Improvements are needed in the thermophysical properties of substances to provide the appropriate plasma process development and optimization. The general data base needs to be improved by:

1. Adding new, plasma-specific data.

Table III. (Modeling Priorities for Various Applications)
(Priorities decrease with increasing number)

Need	Industrial Priorities			University Priorities
	Melt/Smelt	Spray	Synthesis	
1. Arc-melt interaction	1			6
2. Reaction kinetics: homogeneous & heterogeneous			1	3
3. Turbulence with and without particulates	6	1	5	5
4. Arc-Electrode interaction,noise generation, stability	2		7	6
5. Model for variable, 3D Geometry a. with/without cold gas injection b. with/without magnetic fields		2		2
6. Nucleation, growth & agglomeration theory			2	4
7. Experimental data to verify models (flow visualization, heat flow, substrate interaction)	5	3	3	7
8. Thermodynamic and Transport Property Calculation	3	5	4	
9. Radiative Transport	4		6	
10. Plasma-particulate interaction: a. Particulate shape & charge effects b. Non-continuum(rarefied gas) effects c. Particulate-particulate interaction		4	8	1
11. Nonequilibrium effects		6		
12. Compressible flow effects		7		

2. Reducing the scatter in existing data because the model results are directly influenced by the accuracy of the thermodynamic, transport, kinetic and radiative property values.

Property values which are needed are:

1. Thermal and electrical conductivity.
2. Viscosity and diffusion cross-sections.
3. Chemical reaction rates and kinetic data at high temperature for plasma

process gases, e.g. metal vapor and other gas mixtures.
4. Enthalpy of formation.
5. Entropy and specific heats.
6. Optical properties of liquids and solids at high temperatures.
7. Surface tension at high temperatures.

Techniques to properly determine transport properties in boundary layers containing vapors and in steep gradients of concentration and temperature are also needed. Thermodynamic property calculations should include techniques to handle more complex (plasma) mixtures, e.g. include diatomics, etc.

Methods and/or apparatus need to be developed to measure properties at high temperatures. Also needed are molecular calculations based on appropriate intermolecular potentials, models, and other molecular/atomic data to determine:

1. Collision cross sections (especially electron/excited atom)
2. Kinetic reaction rates
3. Energy levels and statistical weights
4. Atomic and molecular transition probabilities
5. Continuum radiation ξ factors

Specific data is needed for atomic and ionic transition probabilities, collision cross sections and reaction rate constants for the lanthanide series, alkali metals, alkaline-earth metals, rare-earth metals and the halogen group. Such studies might also include interactions with Hg, Cd, In, Tl and W. Transition metal electron-atom cross sections are needed because little data is available for either elastic or inelastic cross sections. Most of the available 0.5 eV data is very old and is available mostly for noble gases. Theoretical calculations are complex and have uncertainties of 20%. Present experimental techniques should be able to increase the accuracy and allow a more appropriate determination of electrical and thermal conductivities. Improvements in cross sectional data need to be made in other metallic species, C, N, O and Ar (both atomic and ionic). The latter are important as impurities or bulk media. Other substances which often occur in industrial processes and for which properties should be better known are discussed under Modeling (Ch. 2.3.2) or in survey articles on the production of certain materials.

2.3.4 Specific Research Topics

Table IV presents the priorities of topics in which more basic research into process mechanisms is needed. Most of the topics in Table IV area also included as priority items under Diagnostics, Properties or Modeling. Here, basic research in understanding the process mechanisms is the main issue, whereas in the previous tables, etc. the need for a model (empirical or analytical) or diagnostic tool for some narrow application is desired.

With few exceptions, the priorities in Table IV are rather similar for all the applications. The first item, the characterization of plasmas in actual processing systems, is still judged most important. The third item, related to the interaction of the injected reactants with the plasma is almost as important. The fourth item contains a description of the physical and chemical processes in the reaction zone and is related to the first item. Item five shows that studies of quenching effects have a similar high priority.

Table IV. Priorities for Specific Research Topics in Various Applications

Topic	Melt/ Smelt	Spray	Synthesis Powder	Synthesis Chemical
1. Characterization of plasma incl. turbulence:$\langle T\rangle$,$\langle \delta T^2\rangle$,$\langle V\rangle$,$\langle \delta V^2\rangle$	1	1	1	1
2. Interaction of plasma and liquid electrodes	1			
3. Studies of loading rates, process efficiencies, and product quality loading	2	1	1	1
4. Nucleation and/or growth of particulates; chemical and catalytic effects; particulate definition	2		2	1
5. Effect of quenching techniques on structure and properties	2	2	2	2
6. Dominant interactions among particulates and plasmas, including non-continuum, charge, vaporization, radiation, and dense loading effects		3	3	4
7. Product collection and handling, mechanism of splatting, coating surface phenomena(thickness, temperature, density, composition, bonding, etc.)		3	4	4
8. Studies of parameters influencing effective residence time, particle rajectory, new centerline injection methods, etc.		4	4	4
9. Electrode erosion mechanisms and material improvements	3		6	6
10. Boundary layer transport mechanisms	4			
11. Studies of agglomeration techniques		5	5	
12. Catalytic wall effects				5
13. Particle feeders		5		
14. Influence of arc radiation	5			
15. Multistaged reactor studies			5	5
16. High temperature thermodynamic and transport properties needed			6	6
17. Nucleation seeding studies			7	
18. Plasma jet model validation, incl. heat transfer from jet to surrounding wall		7		

SUMMARY

The major research needs are summarized in Table V as a function of the area and application of specific details regarding the type of research is discussed in the main text. The list in Table V is not all-inclusive nor does it list priorities in an "absolute" sense. The list does indicate present research needs in the view of the participants of the workshop. It should provide an excellent guideline for program managers to weight the relative importance of proposals as well as provide a source of topical research areas for prospective researchers in thermal plasmas.

As an overall summary of priorities to the general thermal plasma area, Table IV indicates the following:

1. Determination of plasma characteristics: composition, gas temperature and velocity, including turbulence.

2. Specification of plasma-particulate interactions, including heat and mass transfer involving non-continuum, charge, vaporization, radiation, trajectory, and dense loading effects.

3. Description of homogeneous and heterogeneous reaction kinetics for nucleation, growth, agglomeration and quenching effects.

4. Development of variable, 3-D geometry models and diagnostics.

5. Calculation and experimental verification of transport, chemical, thermodynamic, radiative and mechanical properties.

6. Experimental validation of models.

2.4 CONCLUSIONS AND RECOMMENDATIONS

The purpose of the workshop was to identify the areas in plasma technology where scientific and/or technological advances would have an impact on this area and, therefore, on processing or manufacturing technology overall. The plasma applications which were selected for this workshop are in a stage where they are particularly suitable for the purpose of this workshop, and the presentations and discussions at the workshop demonstrated indeed that these applications are on their way to the forefront of processing and manufacturing technology. A spreading interest in the industry as a result of numerous marketing and financial studies is a testimony of the promise that plasma applications offer. In the following we list the needs which were identified by the workshop participants as those the satisfaction of which will have the strongest impact on the advancement of the technology. The order of the listing is according to strongest overall impact on all applications considered.

I. Diagnostics of Plasmas in Practical Systems

This means the spatially and temporarily resolved characterization of plasmas with respect to their temperature and velocity distributions, their local composition, and the overall flow pattern. A practical system is not necessarily a full-scale production or prototype system, but a system which includes all the

Table V. Summary of Major Priorities in Thermal Plasma Systems Research.

	Melting/Smelting	Plasma Spraying	Plasma Powder & Chemical Synthesis
Diagnostics:	*Gas composition in arc-melt interaction *Gas temperature in arc-melt interaction *Heat & mass transfer to melt surface *Feedstock particle trajectory *Gas velocity in arc-melt interaction	*Heat & mass transfer to particulates *In-situ techniques for t_{coat} *Gas temperature in the flow *Gas velocity in the flow *In-situ techniques for ρ_{coat} & C_{coat}	*Gas composition in the flow *Gas velocity in the flow *Gas temperature in the flow *Heat & mass transfer to particulates *Feedstock particulate trajectory
Modeling:	*Arc-melt interaction *Arc-electrode interaction *Thermodynamic & transport property calc. *Radiative transport *Experimental validation of models	*Turbulence modeling *Model for variable, 3-D geometry *Experimental validation of models *Plasma-particulate interaction *Thermodynamic & transport property calc.	*Reaction kinetics: homogeneous & heterogeneous *Nucleation, growth & agglomeration theory *Experimental validation of models *Thermodynamic & transport property calc. *Turbulence modeling
Mechanisms:	*Characteristics of plasma,incl.turbulence *Plasma-liquid electrode interaction *Loading rates, efficiency, product quality *Nucleation & growth of particulates *Effect of quenching on product	*Characteristics of plasma,incl.turbulence *Loading rates, efficiency, product quality *Nucleation & growth of particulates *Effect of quenching on product *Plasma/particulate interactions	*Characteristics of plasma, incl. turbulence *Loading rates, efficiency, product quality *Nucleation & growth of particulates *Effect of quenching on product *Plasma/particulate interactions
Properties:	*Transport: Thermal & electrical conductivity, viscosity and diffusion cross sections *Chemical: Chemical reaction rates and kinetic data at high temperature *Thermodynamic: Enthalpy of formation, entropy and specific heat data *Radiative: Optical properties of liquids and solids at high temperatures Energy levels, statistical weights, and line and continuum "transition" probabilities *Mechanical: Surface tension of liquids at high temperatures		

important physical effects, such as strong nonuniformities in plasma temperature and velocity, possibly heterogeneous in plasma composition, with the character of the plasma being influenced by solid or liquid particles. In addition, optical access may be limited by the fact that the plasma mixture is optically thick over a large portion of the spectrum, and data evaluation is made difficult because of the likely lack of symmetry.

The required work would consist of clever adaptation of available diagnostic methods, or possible development of new diagnostic techniques.

The results will be a definition of the parameters for realistic models which, in turn, will allow optimization of reactor design and process conditions. The benefits will impact every application considered, i.e. productivity improvement in metallurgical systems, more uniform particle heating in spraying, improved product uniformity and higher yield in synthesis.

This specific area would benefit more than any other from an additional workshop with a very focussed agenda, concentrating on the conditions in "practical plasmas" and definition of appropriate diagnostics. In particular, it appears worthwhile to investigate what experiences can be transferred from characterization of combustion systems or MHD systems where much work has been done.

II. Models and Model Verification Experiments

Although there was some disagreement about the value of models for the development of practical systems, this disagreement can probably be reduced to differences in the definition of what a "model" consists of. If we include in this definition a semiquantitative correlation of cause and effect, the value of models is universally accepted. The model verification experiments define laboratory-scale experiments to verify effects described by the models. The most frequent criticisms of these experiments by scientists involved in the development of practical systems are (a) that the experimental results cannot be extrapolated because in larger systems other effects may become dominant (e.g. electrode erosion at currents below 1kA and at currents of several kA), and (b) that synergism between two different physical phenomena may produce a different effect in practical systems (e.g. catalysis). Design of the experiment will have to consider these criticisms. The specific models are ranked with regard to their overall impact on the considered applications as seen by the workshop participants.

(a) Interaction of the plasma with the feed stock, i.e. interactions with a cloud of particles, with a large number of chips, or with a cold gas of a different composition. The major question here is the scaling of existing models describing single particle-plasma interaction to realistic conditions.

The benefits would be optimization of feed rates and, therefore, operational efficiency for plasma spraying and several of the metallurgical applications, but also for chemical synthesis applications.

(b) Plasma-single particle interaction, i.e. description of heat, mass and momentum transfer. Very much is being done in this area including work by several of the workshop participants. The results are seen to benefit plasma spray applications by defining torch design and operating

parameters for most efficient and uniform particle heating, but also the metallurgical applications where the feedstock is added as fines through the plasma. Obviously, these types of models are a precursor to the model described in (a).

(c) Reaction kinetics models and determination of rate coefficients. These models will have to replace the common equilibrium models for accurate prediction of process yield as function of reactor design and operation. The applications benefiting from these efforts will be predominantly powder synthesis and chemical processing including waste destruction.

(d) Nucleation and particle growth under plasma conditions. An understanding of these physical processes is of critical importance to plasma synthesis of submicron particles, in particular ceramics. The results of efforts in this area will lead to optimal reactor design and operation for maximum product uniformity. They may even lead us to synthesis of so far unknown phases of materials with attractive properties.

III. Plasma-electrode Interaction Studies

These studies are crucial for the majority of the metallurgical applications, but also important for the chemical processing application. The effects to be considered include magnetic effects which are important at high currents in the plasma as well as in the electrode, chemical reactions between molten metal and the plasma which occur at high current densities with solid and liquid electrodes, and the momentum transfer between the high current arc and a liquid electrode. The results will have an important impact on the development of high-power plasma torches, needed for the metallurgical industry, but also for the operating life of the electrodes in present installations, i.e., the efficiency of their operation, and on the process optimization of current open hearth melting furnaces.

IV. Plasma Systems Considerations

Under this heading fall the items which are not directly related to plasmas, but are important to some plasma applications.

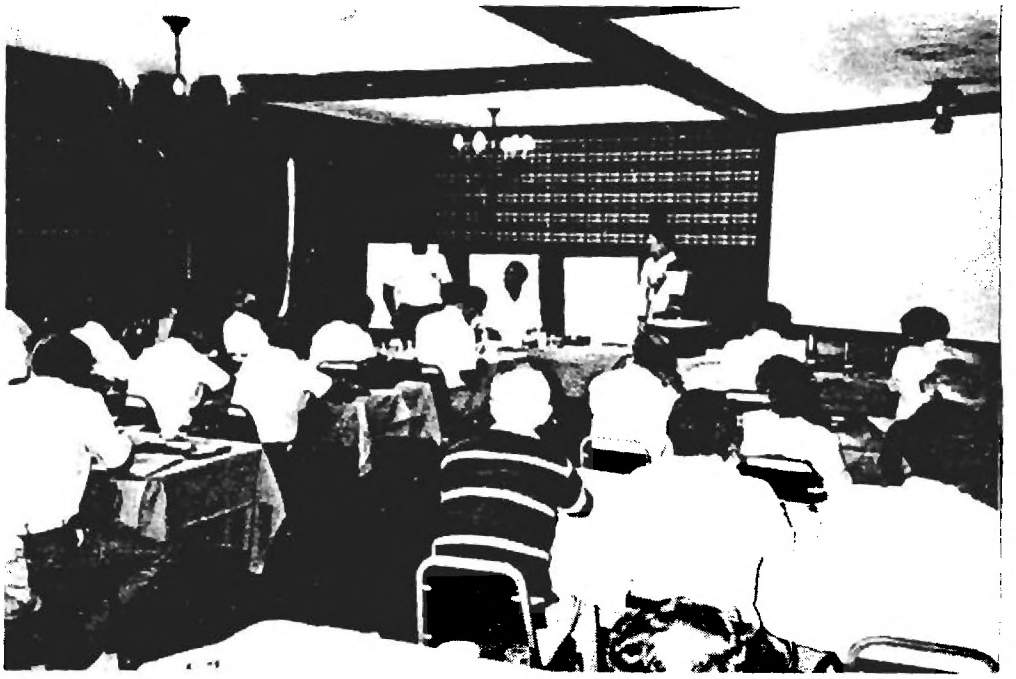
(a) Powder product collection and handling of plasma-synthesized, ultra-fine particles. The value of the plasma produced powders for further processing, e.g. sintering to ceramic structures, is dependent not only on what has happened in the plasma region, but also on any changes that might occur in the handling, e.g. the kind of agglomerations that form, or the surface oxidations that may occur.

(b) Particle splatting on a substrate is an important part of the plasma spray process, and identification of the important parameters influencing this splatting such that a smooth film will be generated may lead to making such coatings attractive for more and more applications.

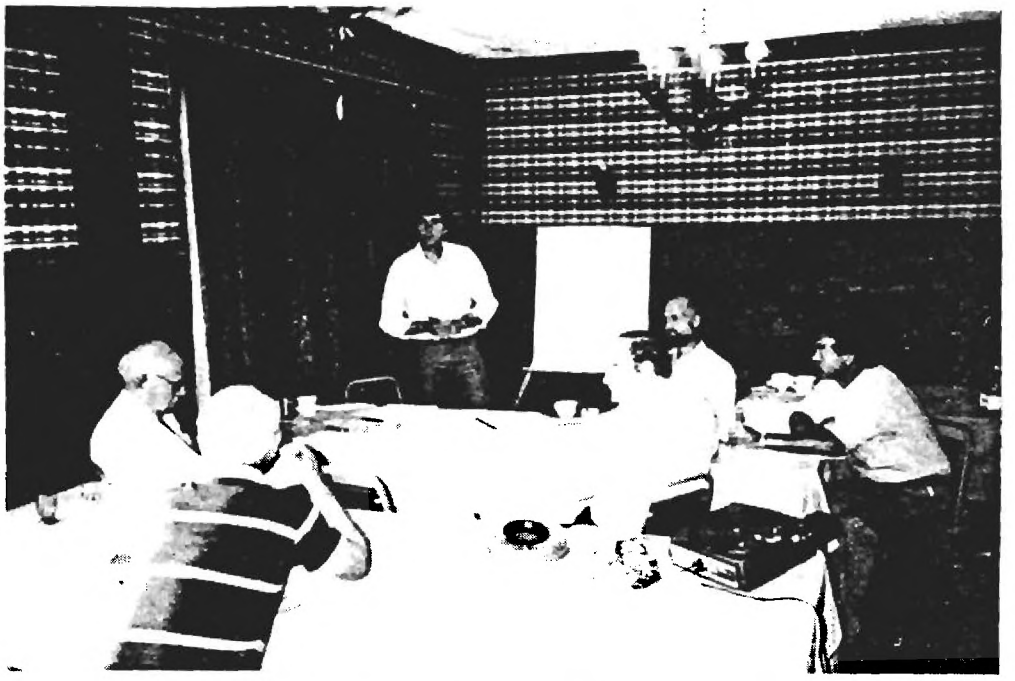
V. Additional Workshops

Finally, we recommend that a workshop on "diagnostics in practical high temperature systems" be held to identify more specifically funding priorities in this important area.

With regard to the other items on the list, the ranking did not consider that some of the identified tasks may already have a considerable amount of funding through the Manufacturing Technology Program of the U.S. Department of Defense (e.g. some plasma spraying related work). Otherwise, research in all identified areas promises to have an impact on industrial productivity and competitiveness and is, therefore, recommended for support.



Presentations of the State-of-art for thermal plasma systems.



Webster Room Discussion Group. Left to right: J. Elliot, E. Pfender, M. McIlwain, N. Barcza, D. Houck, and H. Anderson.

THERMAL PLASMA TECHNOLOGY

CHAPTER 3

MELTING AND SMELTING OF METALS

Session Chairman

D. Mac Rae
Research Center
Bethlehem Steel Corporation
Bethlehem, Pennsylvania 18016

3.1 ARC FURNACE MELTING: TRANSFERRED MODE

D. NEUSCHÜTZ
Friedr. Krupp GHBH, Forschungsinstitut
Münchener Str. 100
D 4300 Essen 1, W. Germany

The steel industry is of particular interest to plasma technology, because it represents the largest potential market combined with a need to improve production technology. Presently, about 25% of all the steel is produced by arc furnace remelting and modern plasma furnaces are aimed at replacing the conventional submerged arc furnaces in this market segment. The driving force for introducing plasma furnace technology are the need for improved product quality and process productivity. In modern plasma furnaces an arc is sustained between a nonconsumable electrode and the metal melt. A noble gas flow stabilizes the arc. Two specific configurations are shown in Fig. 1. In Fig. 1a, the arc has a stationary attachment to a hot electrode, whereas Figure 1b depicts a cold electrode where typically a magnetic field is used to rapidly rotate the arc attachment and distribute the heat flow to the electrode. Both configurations can be designed to operate on either AC or DC. The major advantages of the plasma furnace are:

(1) Improved process control because the process chemistry is decoupled from the heating;

(2) Less acoustic noise pollution and less electrical noise fed back into the power grid;

(3) Almost negligible electrode erosion compared to arc furnaces operating with (expensive) consumable graphite electrodes;

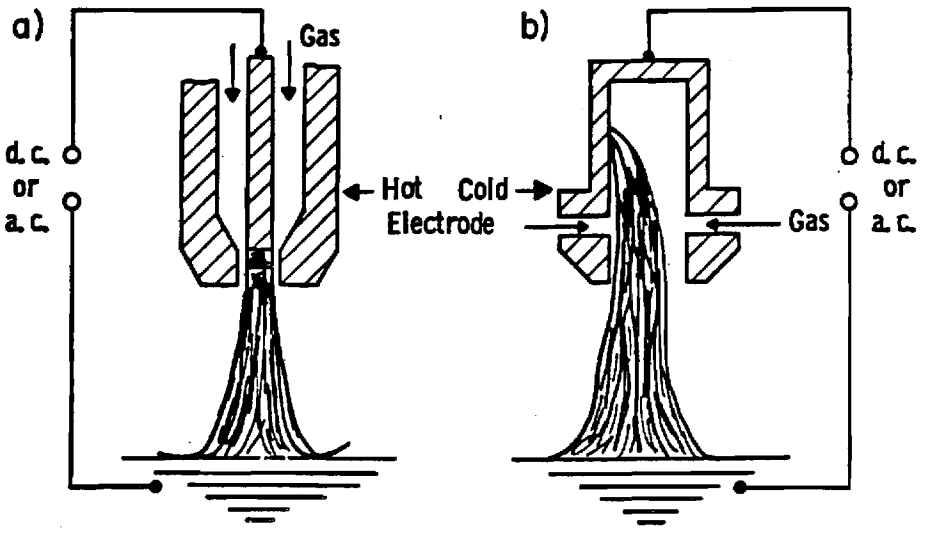


Fig. 1 Gas stabilized transferred arc plasma torches for heating solid and liquid material.

Table I. Plasma Furnaces in Operation and under Development

Location	Size tons	Purpose	Plasma Heaters No and Current Rating (Supplier)	Year of Start-up
Freital, GDR	15	scrap melting		1973
Freital, GDR	35	"	3 x 7 kA DC	1978
Voest, Austria	45	"	4 x 9 kA DC	1983
Krupp, FRG	3	"	3 x 4 kA AC	1982
Krupp, FRG	10	"	3 x 6 kA AC	1986
Krupp, FRG	50	ladle heating	3 x 6 kA DC	1987
Nippon Steel Japan		Liquid Steel in tundishes	5 kA DC (Tetronics)	under test
PEC, USA		"	(PEC)	"
Tetronics, UK		melting of fines (EAF dust)	under test	
Retech, USA		(re) melting of Ti,Ni alloys	[Several production furnaces available]	
Texas Gulf, USA		melting of automotive catalytic converters (Tetronics) for Pt-recovery (30% of US production)		

A disadvantage is the need for a supply of noble gas (argon). Plasma furnaces in operation and some of their characteristics are shown in Table I.

Figure 2 shows the size of the plasma heater required for a given melting furnace/ladle capacity, assuming three torches per furnace operating in three phase. Power requirements for plasma furnace melting are presently 0.5 MW/ton, and presently obtained heating rates for ladles are 3 °C/min. Economics will require the use of torches with higher current ratings.

The large number of independent parameters (or almost independent) allow the optimization of the process under consideration, but also make this optimization process rather complex. The parameters are: gas type and flow, arc current, power supply design, method of arc ignition, electrode type, material and cooling, and nozzle design. The general areas requiring research are: electrode wear, nozzle wear, control of stray arcs and arc stability, noise emission, electric noise generation, interaction of plasma jet with the melt, heat transfer from the plasma to the surroundings, and diagnostic investigations of the arc plasma, e.g. determination of the different species in the plasma. Specific research topics which would have a direct impact on the plasma melting technology and in which one needs advances for the extended application of transferred arc plasma systems as heating and melting devices are:

- Investigate arc-electrode interaction phenomena at high currents (2kA to 25kA) for AC and DC arcs required for scale-up of high current plasma torches with acceptable electrode life.
- Achieve understanding of the dominant heat transfer mechanisms in industrial furnaces to improve the thermal efficiency.
- Minimize the plasma gas consumption to reduce operating cost and improve pollution.

- Develop thermal, electrical, physical and chemical models for the plasma process and system to assist in furnace design, process control and optimization.

- Investigate plasma-melt interactions (thermal, physical and chemical) to improve process control and to identify new plasma furnace applications.

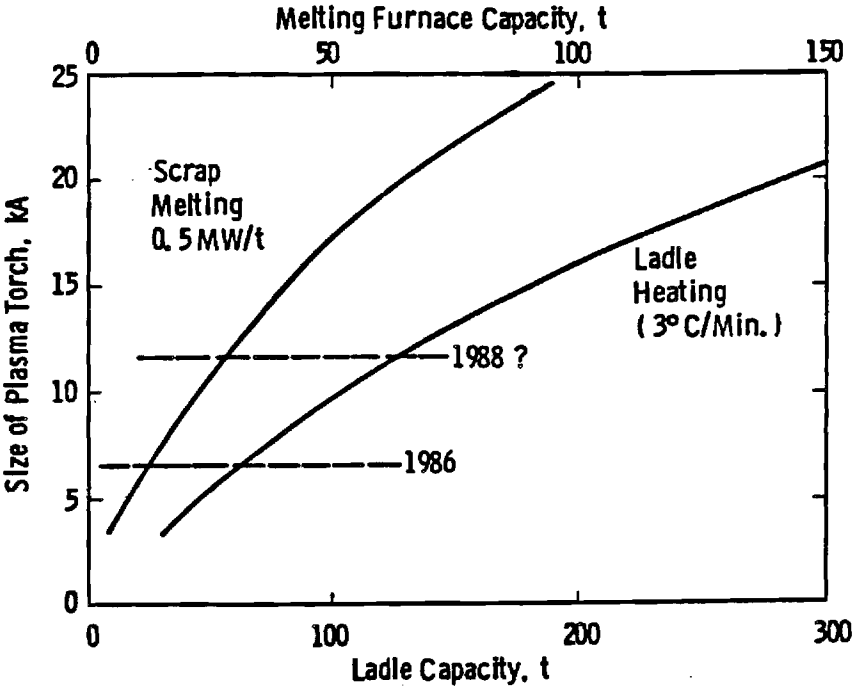


Fig. 2. Plasma torch sizes needed for steel melting and heating, assuming 3-phase, 3-torch operation.

3.2 ARC FURNACE SMELTING: TRANSFERRED MODE

N. A. BARCZA
Pyrometallurgy Division
Mintek
Private Bag X3015
Randburg, 2125 South Africa

Definition of System Geometry

The plasma torch is normally located above the surface of the bath and is vertically positioned in most systems although inclined torches are used in some instances. The open bath surface implies that there is no solid lumpy burden covering the upper region of the furnace, unlike the case of the conventional submerged-arc furnaces (or shaft furnaces) where the charge forms a permeable layer that permits the gaseous reaction products to escape (typically CO and a little CO_2). The bath and plasma torch are contained in a refractory-lined vessel that is made from mild steel. The refractories are chosen to have a suitable thermal conductivity and high temperature resistance (thermal).

The feed materials, normally comprising an ore, fluxes and a reducing agent, e.g. coke or coal, are gravity-fed onto the surface of the liquid bath via a feed port in the roof of the furnace. The reaction products of metal and slag are tapped in a batch manner while the feed is introduced continuously. The off-gases are removed via an exhaust port in the roof prior to dust removal in the conventional manner.

Process Chemistry

Inputs: These comprise solid feed ore, normally as an oxide (MeO), fluxes to form a low liquidus slag phase containing the nonreducible oxides (e.g. silica, or lime) and a reductant, normally solid carbon in the form of coke or coal. The other major input is the thermal energy that is generated by the electrical energy of the thermal plasma. The energy is required by the endothermic reduction reactions that take place in the liquid bath.

Reactions: These comprise melting of the feed materials, in particular the oxide ore and the fluxes. Dissolution of the various oxides takes place in the slag phase and reduction of the reducible oxides occurs, e.g. carbothermic reduction if carbon is used, aluminothermic if aluminum is used, or silicothermic if silicon is used.

Products: The products are either metals or carbides, a slag containing the unreduced oxides and the off-gas.

The overall reaction can be depicted as follows:

$$MeO + C = Me + CO$$

A major advantage of using plasma as the source of thermal energy for such reactions is the independence of the energy from oxygen potential (P_{O2}) unlike combustion which is not P_{O2} independent. This allows the reduction of stable oxide ores to be achieved.

Process Parameters

To control the reactions that take place in an open bath transferred plasma arc system particular attention has to be paid to the following: Feed rate and feed distribution, power input level, the energy balance based on the thermodynamic requirements and taking the heat losses from the system into account. The energy distribution over the bath is also of importance. The overall electrical-to-thermal efficiency determines the through-put that can be attained for a given power input level.

Equipment Parameters

The major factors that determine the performance and scale-up potential of a transferred-arc plasma system are the power capability of the plasma torch, the integrity of the anode in the bath, the refractory design of the roof and side walls, the stability of the plasma arc column, especially with regard to stray arcs, arc flare, and arc skewing.

Operating characteristics that determine the performance of the system include the current and voltage levels, the gas type and flow rate, and the electrode wear rate. These characteristics are very different for non-transferred-arc systems as compared with transferred-arc systems discussed here, the latter being high current, low voltage, low gas requirement, and a relatively high electrode wear rate.

Applications

Commercial applications for transferred-arc systems are ferrochromium (FeCr) where a 16 MVA d.c. arc furnace with a hollow graphite electrode is used as the cathode and through which the feed materials are introduced for smelting or melting, and ferromanganese (FeMn) where a 10 MVA furnace, using a water-cooled metallic torch, is employed for melting metal fines.

Applications under development include: ferrosilicon (FeSi), silicon (Si), ferrovanadium (FeV), vanadium (V), vanadium carbide (VC), ferrotitanium (FeTi), titanium aluminide (TiAl), titanium (Ti), magnesium (Mg) and aluminum. Many of these are still at an early stage of development, however.

Research Suggestions

A. Look at the rate-determining factors.

To increase efficiency and thus throughput, it is important to gain an improved understanding of whether the process is:

1. Energy-transfer rate limited.
2. Energy distribution limited.
3. Reaction rate limited.
4. Mass transport limited.

B. Experimental approaches

Testwork should be carried out to measure the effect of the following parameters on the rate-limiting aspect of the process, namely,

1. Increase of power density (MW/m^2 bath area),
2. Spread or distribute energy input over bath,
3. Decrease particle size of feed materials, and
4. Stir bath to improve mass and heat transfer.

C. Theoretical approaches

In addition to experimental work, modeling of the open bath system, in particular the region of arc attachment, is recommended. The following should be considered:

1. Analyze numerically the energy transfer to and within the bath region.
2. Model the relationship between the diameter of the bath and the power density.
3. Study and model the dissolution kinetics of the feed, in particular the oxide ore.
4. Study and model the reduction mechanism.

Conclusions

In conclusion, the major advantages of plasma are:

1. Cost savings, both capital and operating.
2. Improved product quality, i.e. specification.
3. New products not possible in conventional processes.

3.3 ARC GENERATOR SMELTING AND MELTING: NONTRANSFERRED MODE

J. FEINMAN
Consultant
2654 Sperber Lane
Grand Junction, CO 81506

Applications of nontransferred arc plasma generators to smelting and melting ferrous ores and metals are among the most advanced applications of high-power plasma energy from a commercial standpoint. Figure 1 shows how the nontransferred and the transferred arc generators are applied to smelting and melting in a schematic manner. The nontransferred systems are generally designed to operate as countercurrent shaft reactors which are usually charged with coke at the top. The transferred arc systems usually operate in an open-bath mode with free space above the slag/metal baths above the hearth. The following discussion will concentrate on the nontransferred arc applications that have been developed to commercial or near-commercial status and therefore are representative of the state-of-the-art in this technology.

Some of the common features shared by the nontransferred and transferred arc systems are summarized in Table I. Important differences between the systems are listed in Table II.

Figure 2 is a schematic diagram of the plasma-fired cupola developed by Westinghouse Electric Corporation in cooperation with Electric Power Research Institute, Modern Equipment Company and General Motors - Central Foundry Division [1]. After a successful test program plans for a commercial installation at General Motors - Central Foundry Division are being implemented. The advantages of the plasma-fired cupola for melting steel scrap include lower coke consumption,

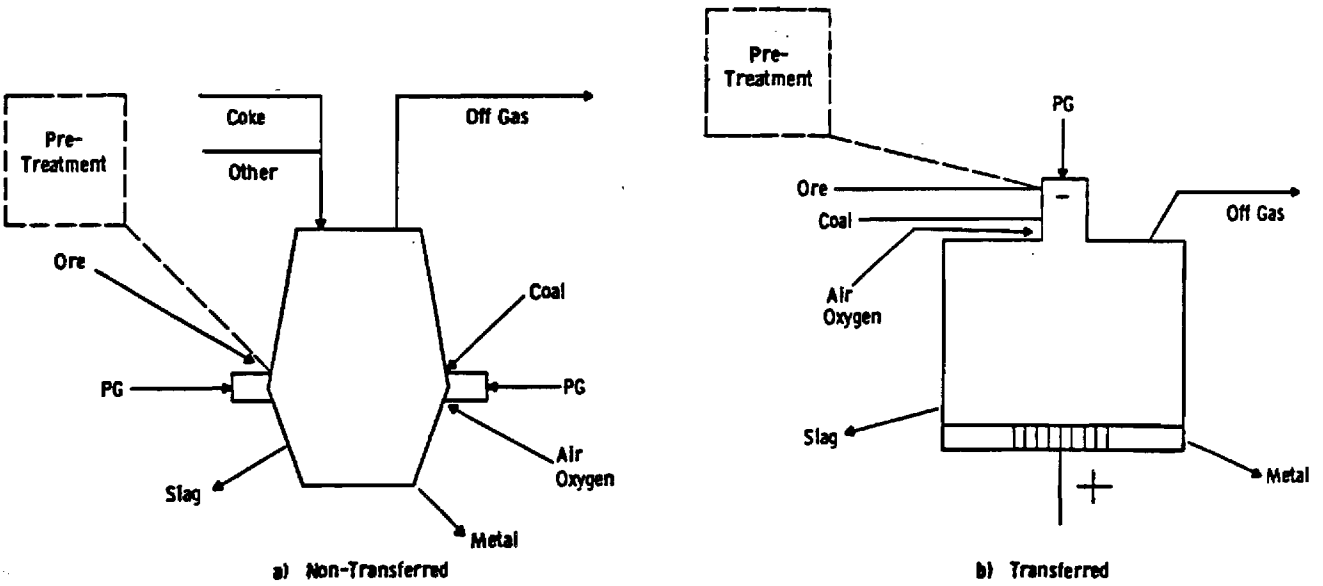


Fig. 1. Schematic arrangement of non-transferred and transferred arc smelting installations.

Table I. Common Features of Transferred and Nontransferred Arc Plasma Generators

- FINE ORES AND CONCENTRATES
- COAL FOR REDUCTANT AND FUEL
- ENERGY FROM PLASMA AND FOSSIL FUELS
- DIRTY OFFGAS
- DRYING, PREHEATING, PREREDUCTION
- CLEAN RECYCLE FOR PLASMA GAS

higher productivity and the ability to charge turnings and other small-sized scrap without briquetting because gas velocities in the shaft are lower than with conventional practice.

Other processes based on the coke-filled shaft reactor that have reached the commercial stage include the PLASMADUST process for treating waste steel plant dust and the PLASMACHROME process for producing ferrochrome, both developed by SKF Steel Engineering AB in Hofors, Sweden. A plant based on PLASMADUST has been in operation at Landskrona, Sweden since 1984 [2]. This plant, operated by ScanDust AB, is powered by three 6-MW plasma generators and can treat 70,000 tons of waste dust per year to recover zinc and lead and a high-alloy metal that is suitable for recycle to stainless steel manufacturers. The remaining constituents are converted to an inert glassy slag that is suitable for road ballast. A plant based on the PLASMACHROME process was started up in July 1986 in Malmö, Sweden [3]. This plant, operated by SwedeChrome AB, comprises two shafts, each powered by four 6-MW plasma generators and is designed to provide 77,000 tonnes per year of high-carbon ferrochrome from fine chromium ores.

TABLE II. Differences between Transferred and Nontransferred Arc Plasma Generators

NONTRANSFERRED	TRANSFERRED
TOP FEED, LUMPS LOWER OFFGAS T	HIGH OFFGAS T
FILTERING EFFECT OF COKE	----------
LOW PLASMAGAS ENTHALPY HIGH VOLUME OFFGAS	HIGH PLASMAGAS ENTHALPY LOW VOLUME OFFGAS
HIGHER ENERGY/CARBON HOLDUP "NONCRITICAL" INPUT CONTROL	LOW ENERGY/CARBON HOLDUP "CRITICAL" INPUT CONTROL
CONVENTIONAL REFRACTORY CONDITION	SEVERE REFRACTORY CONDITION
LOW OXYGEN POTENTIAL (EXCEPT FUMER & MELTER)	FLEXIBLE OXYGEN POTENTIAL

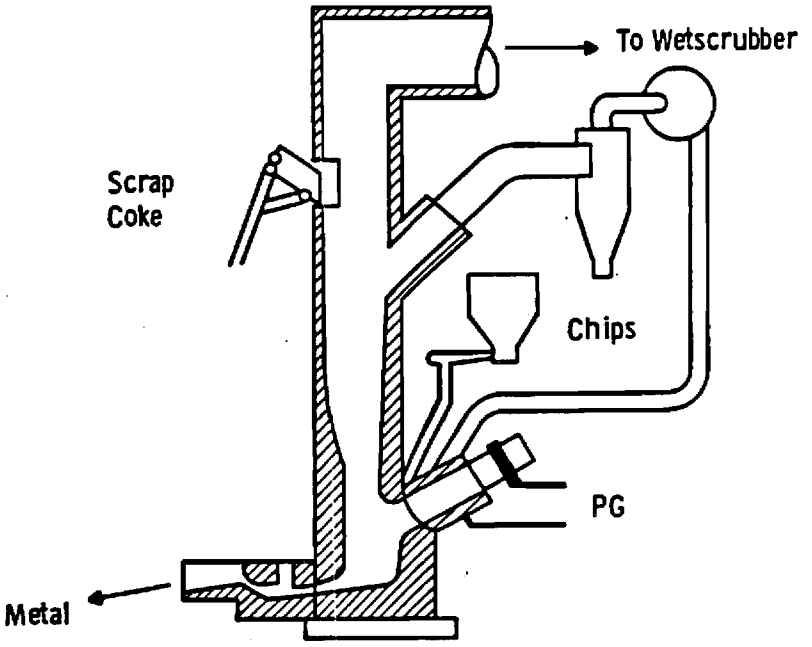


Fig. 2. Schematic of a plasma-fired cupola for chip melting.

Other processes based on nontransferred arc plasma generators that have reached the commercial stage include those that use plasma energy to produce reducing gas for direct reduction by reforming/gasification of hydrocarbon/carboniferous fuels, and those that use plasma energy to preheat air for blast furnaces. The reforming applications include the PLASMARED process installed by SKF Steel AB at their Hofors plant, which uses one 6-MW plasma generator to reform coal/water slurry to produce CO and H_2 for a 50,000 tonne per year direct reduction shaft [4]. This plant, which was the first commercial application of SKF's 6-MW plasma torches, has been shut down for economic reasons. The other direct reduction application is the plant of the Union Steel Corporation of South Africa, commissioned in 1985, which uses plasma generators of the Huels design to reform synthesis gas from Sasol to produce CO and H_2 for a direct reduction shaft based on the Purofer DR technology [5].

The blast furnace hot-blast heating application is represented by the installation of three 1.5 MW Aerospatiale plasma torches on the ferromanganese blast furnace of Societé Ferromangan de Paris-Outreau (SFPO) in France in 1984. This first commercial installation was highly successful and was followed up by the addition of six additional 1.5-MW generators on this furnace (9 of the 14 Tuyeres) in 1986 [5]. The use of plasma energy to heat blast-furnace hot-blast air has the advantages that expensive coke is replaced by cheaper electrical energy (in locations where the cost ratio is favorable) and additional substitution of cheaper injected fuels for coke is possible. Other promising applications of plasma energy in metallurgical processing include a shaft melter for steel scrap illustrated in Fig. 3 [6] and a "slag-fuming" type reactor shown in Figure 4 [7]. In the melter, plasma energy provides the heat of melting, and complete combustion of coal with air provides the preheating. The total energy requirements are estimated to be about 150 kWh and 70 kg of coal per

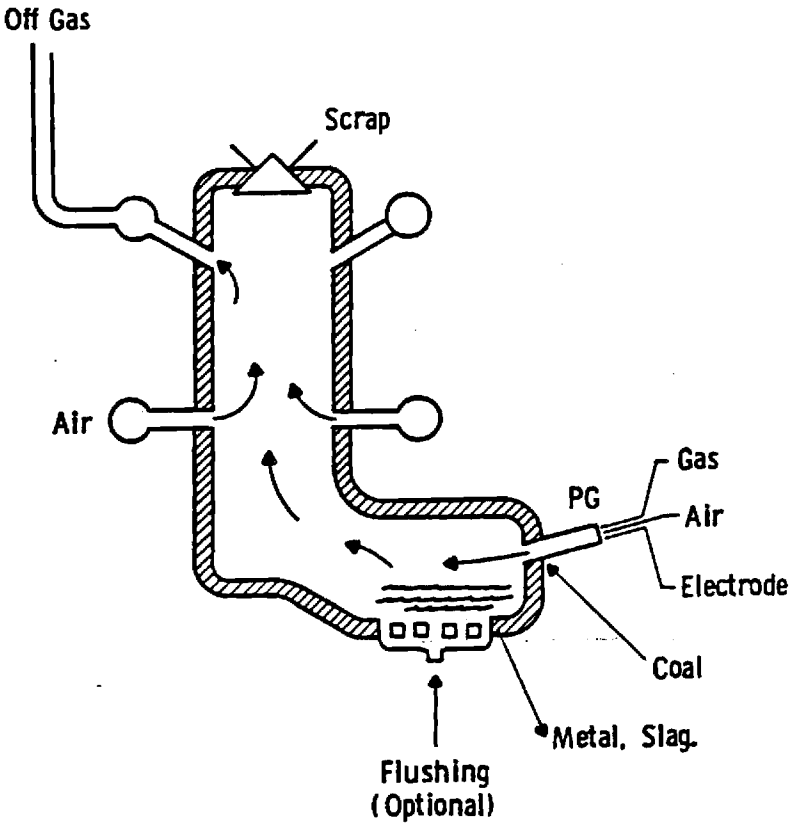


Fig. 3. Schematic of a scrap-melting furnace.

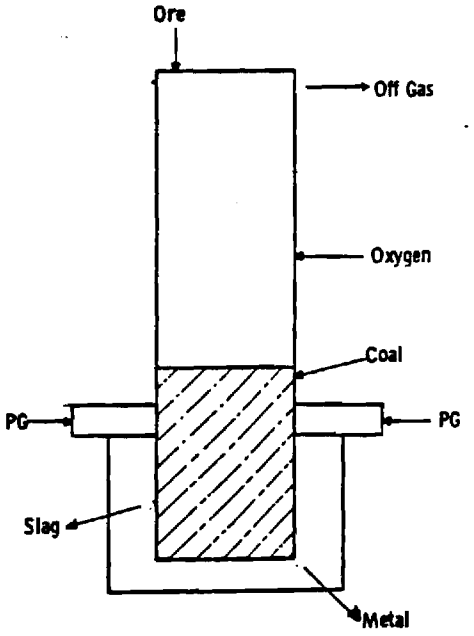


Fig. 4. Schematic of a slag-fuming reactor.

Table III. Problem Areas and Areas for Research and Development

1. PROCESS CONTROL, TRANSIENT EFFECTS.

2. ALKALI DISPOSITION, ESPECIALLY IF OFFGAS IS USED FOR PRETREATING. DEFINITION OF LIMITATIONS AND/OR METHODS FOR CONTROL, e.g., ACID SLAGS. TECHNICAL AND ECONOMIC ANALYSIS.

3. EFFECTS OF GEOMETRY, ETC. ON COAL/PLASMA MIXING AND REACTIONS, TUYERE WEAR. SPONSORED PROGRAM LIKE COMBUSTION RESEARCH AT IJMUIDEN.

4. ELECTRODE EROSION STUDIES.
   EFFECTS OF:
   - MATERIALS (ALLOYS), GASES.
   - COOLING RATES AND CONFIGURATION.
   - MAGNETIC FIELDS.

5. MARKET ANALYSIS (U.S. and INTERNATIONAL), ECONOMICS.

tonne of scrap, much less than conventional electric furnace melting or cupola melting. In the "slag-fuming" type reactor, the plasma gas is introduced below the level of a slag bath, which is also injected with pulverized coal. The reduction reactions occur in the slag bath and CO and H_2 produced are combusted to the desired degree of completeness in the freeboard above the bath to provide the energy for preheating the fine ore fed at the top. This system is particularly suited to processing ilmenite and to producing low- or medium-carbon ferrochromium from chromium ores because of the ability to control the oxygen potential in the system without the presence of a coke-filled volume.

General problem areas that could be studied effectively by university staffs/facilities or by independent research/development/engineering organizations are presented in Table III. It should be recognized that none of these recommended projects are essential to commercial expansion for the smelting/melting applications, but all of them would be important to potentially more rapid implementation and to more efficient design and operation.

References

1. S. V. Dighe, W. H. Provis, B. Buczkowski, W. J. Peck and A. K. Karp, "Plasma-Fired Cupola: An Innovation in Iron Foundry Melting," a copy of this unpublished paper may be obtained from Dr. Dighe at Westinghouse Electric Corporation, Box 286, Madison, PA 15663-0286.

2. H. G. Herlitz, "Plasma Technology for Metal Recovery from Oxidic Waste," 1984 Vacuum Metallurgy Conference on Specialty Metals Melting and Processing, Pittsburgh, June 11-13, 1984.

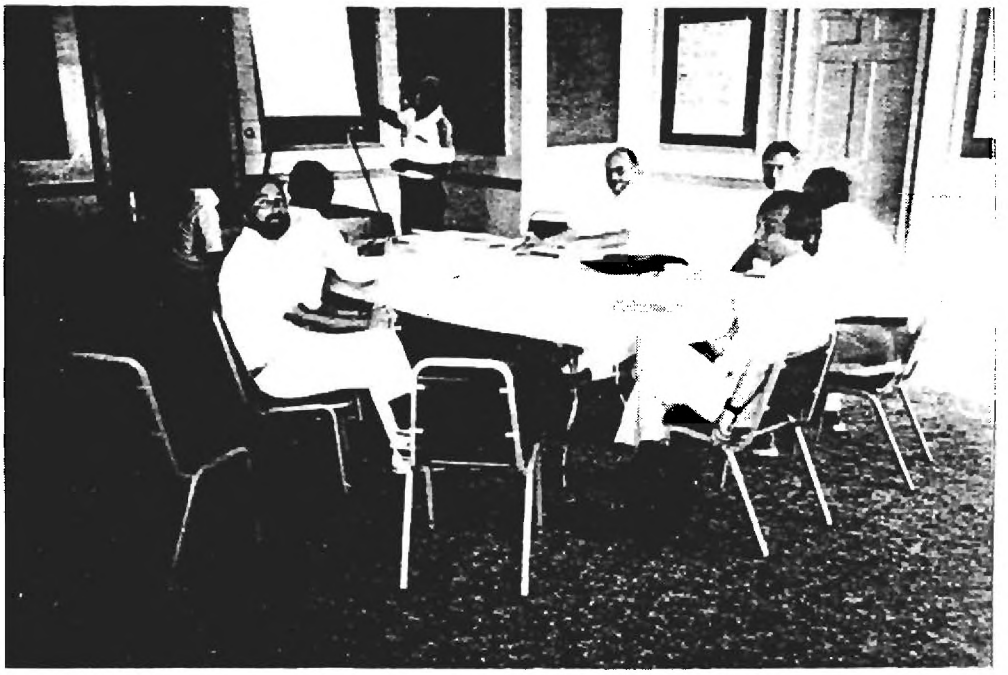
3. C. T. McClelland and S. B. Lasday, "Plasma Furnace Production of Ferrochrome -- A Most Significant Development," Industrial Heating, Vol. LIII, No. 8, August 1986, pp. 18-22.

4. H. G. Herlitz and S. O. Santén, "Production Experience with Plasma Technology in Metallurgical Processing," Iron and Steel Engineer, August 1985, pp. 64-67.

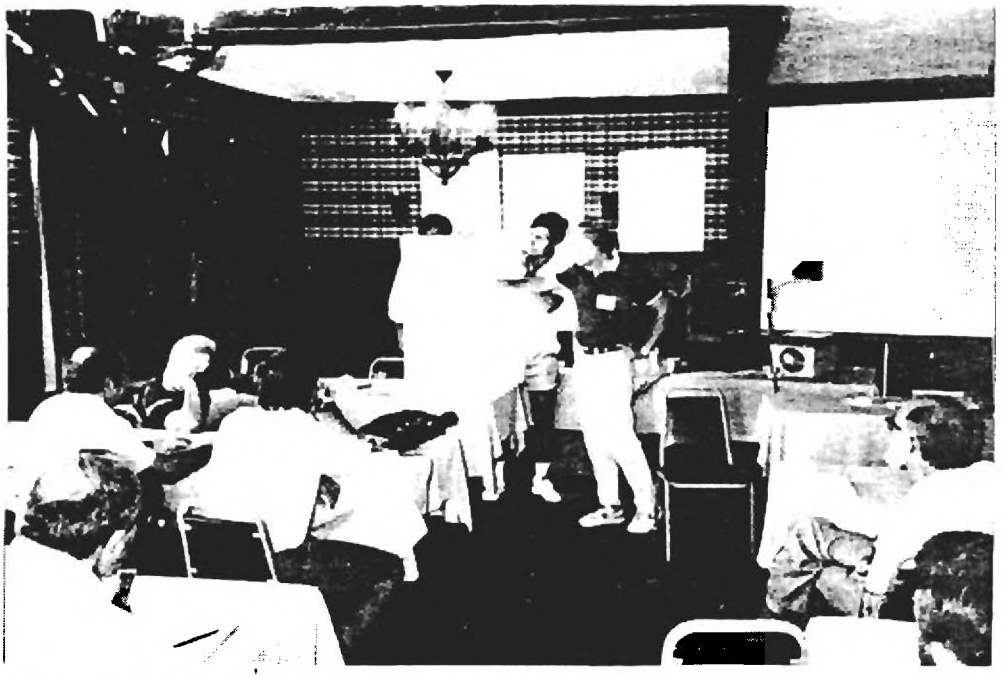
5. Applications of Plasma Technology in Metallurgical Processing, Chapter 9, Editor, J. Feinman, Iron and Steel Society of AIME, Warrendale, Pa., 1987.

6. S. Santén, Canadian Patent 1,043,575, Method and Device for Melting.

7. S. Eriksson, J. Feinman and S. O. Santén, U. S. Patent 4,601,752.



Adams Room Discussion Group. Left to right: C. Cremers, J. Conrad, R. Munz, C. Holden, P. Fauchais, T. Yosida, T. Eddy and D. Mac Rae.



Summary discussion of topical area. Left to right: P. Fanchais, N. Barcza, E. Pfender, M. McIlwain, M. Boulos, T. Meyer, H. Casey, C. Holden and D. Harris.

THERMAL PLASMA TECHNOLOGY

CHAPTER 4

SPRAYING OF METALS AND CERAMICS

Session Chairman

D. Mac Rae
Research Center
Bethlehem Steel Corporation
Bethlehem, Pennsylvania 18016

4.1 PLASMA SPRAYING SYSTEMS

D. HARRIS
APS Materials
153 Walbrook
Dayton, OH 45405

In plasma spray systems, a ceramic or high temperature alloy powder is blown into the high temperature plasma which is generated by a high intensity arc. The high velocity plasma flow entrains the particles and accelerates them towards a substrate. The plasma consists typically of a noble gas, but H_2 or N_2 are also used. The heat transfer from the plasma to the particles must be sufficiently high to melt the particle in the short time of flight before it hits the substrate. Fig. 1 shows a schematic of a typical plasma spray system. Typical process characteristics are listed in Table I. The particles form a film on the substrate which will protect the substrate against adverse environment. The major applications are in the aerospace industry, e.g. for coating of aircraft engine parts. The coating may give either superior thermal properties to a good structural material, or it may give the superior hardness and erosion and oxidation resistance of a superalloy to an inexpensive substrate, saving 80 to 90% of the expensive material.

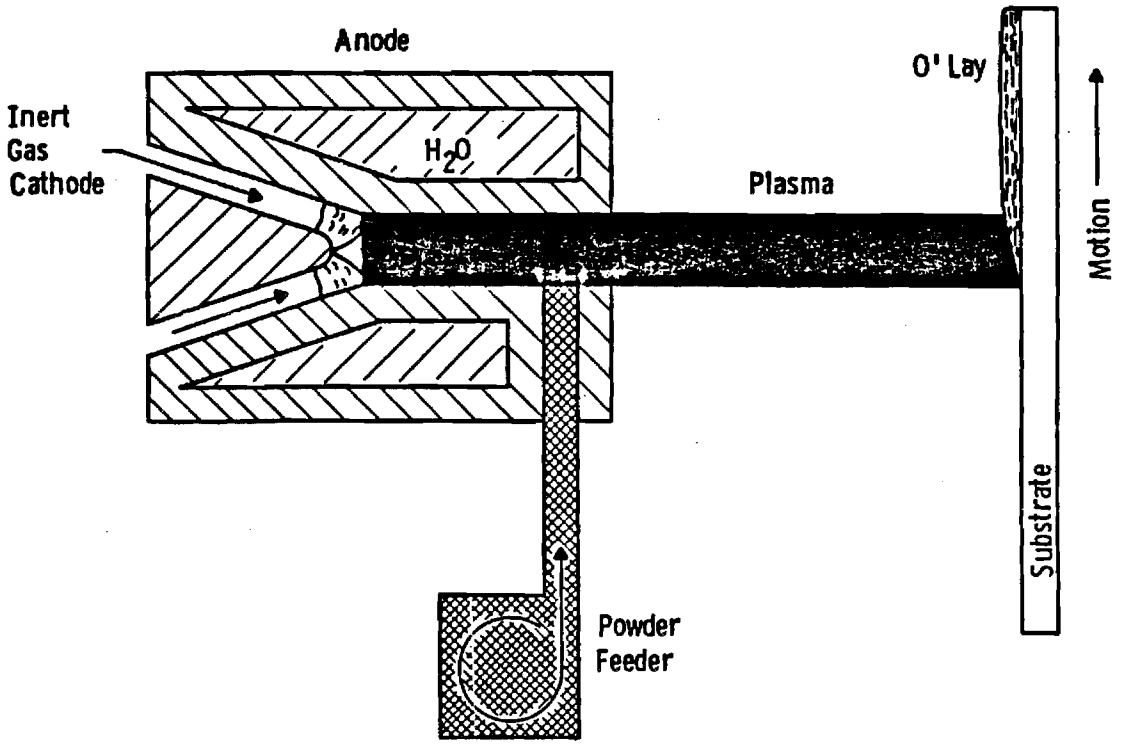


Fig. 1. Schematic of plasma spray torch

Table I. Typical Plasma-Spray Process Characteristics

Material:	Any melting inorganic
Deposition rate:	< 2 oz/hr to > 20 lbs/hr
Substrate temperature:	< 100F to desired
Substrate area:	< 0.003 in^2 to > 100 ft^2
Film density:	88% to > 99% of theoretical
Bond strength:	4000 psi to > 10,000 psi
Micro structure:	generally hyper-fine grain, layered structure with mechanical or quasi-metallurgical bond

The total market in the U.S. for plasma spray coatings was estimated to be about $500M in 1983, with approximately $350M of it in the aerospace industry ($20k worth of plasma spraying in one jet engine), $50 to 75M in the oil drilling industry, and the remainder in the heavy industry. However, applications are increasing in such diverse industries as chemical and paper and metal processing. Thermal resistance coatings or protective overlays against contamination are the major applications in these industries. The automotive industry is a large potential market. Thermal barrier coatings of cylinder walls that also offer increased wear resistance have proven superior in some cases to solid ceramic engines at a much lower cost, and the spray-cast exhaust manifolds exhibit better microstructure and better geometry control than the competitive process of slip casting. The other major growth is seen in the electronics industry for dielectric films, metallization, and for protective overlays. A special application is seen in the medical industry, where a porous coating on an orthopedic implant leads to good fixation to the adjoining bone tissue. Artificial hip and knee systems, but also orthodontic implants provided with a plasma spray coating have been used successfully. A new development with great promise is near net shape manufacturing, where e.g. a turbine blade is built up entirely of plasma spray coatings requiring minimal machining. Considerable savings of expensive materials are realized in this process, in addition to various machinery expenditures.

The technological advances needed for a continued growth of this plasma application are:

- higher reliability (overlays without voids),
- improved coatings with higher intrinsic strengths,
- overlays with a smoother texture,
- spray torches with higher throughputs and higher efficiency.

The research needed to obtain these advances can be divided into three categories:

A. Understanding of what is happening during the impact of the molten particle on the surface;
B. Understanding of the interaction of the particle with the plasma; and
C. Plasma spray equipment design for optimum control of the spray process.

The specific research tasks envisioned are:

1. Electrode nozzle design

   (a) arc stability
   (b) long electrode life
   (c) optimum particle velocity
   (d) effects of operating parameters

2. Instrumentation for real time control

   (a) plasma flow enthalpy
   (b) particle or gas velocity
   (c) feed injection rate

3. Novel torch designs

   (a) dual opposed jets
   (b) low pressure plasma spray systems

4. Spray torches for specific application:

   (a) miniature units for precise overlay placement
   (b) high throughput units for RJR fabrications
   (c) ultra-high velocity units for optimum overlays with cermets

THERMAL PLASMA TECHNOLOGY

CHAPTER 5

SYNTHESIS OF POWDERS

Session Chairman

T. N. Meyer
ALCOA Technical Center
Alcoa Center, Pennsylvania 15069

5.1 IN-FLIGHT PLASMA PROCESSING OF POWDERED MATERIALS

DAVID HOUCK
GTE Products Corp.
Hawes Street
Towanda, PA 18848-0504

In-flight plasma processing of materials is used at the Chemical and Metallurgical Division of GTE in two ways: (1) in the plasma melting and subsequent rapid solidification of the particles, and (2) in a patented plasma micro-atomization technology.

In in-flight processing, spray drying is used to produce agglomerates of fine particles. The agglomerates can contain either elemental powders or fine particles of master alloys. The agglomerates are then passed through a specially designed plasma device to melt, homogenize and/or alloy the constituents. Many alloy systems have been evaluated, e.g., nickel alloys, iron alloys, aluminum alloys, tungsten-rhenium alloys, molybdenum-cobalt alloys, and other molybdenum alloys. The widely acknowledged benefits of the rapidly solidified powdered materials are:

- enhanced magnetic properties,
- improved wear and cutting tool life, and
- increased material strength.

One reason for these benefits is that the plasma melted particles have spherical shapes which allow more efficient packing of the material and, therefore, results in better flow properties and increased bulk densities. An example of a plasma melted composite powder in which titanium carbide is incorporated in a nickel-chrome matrix, is shown in Figure 1.

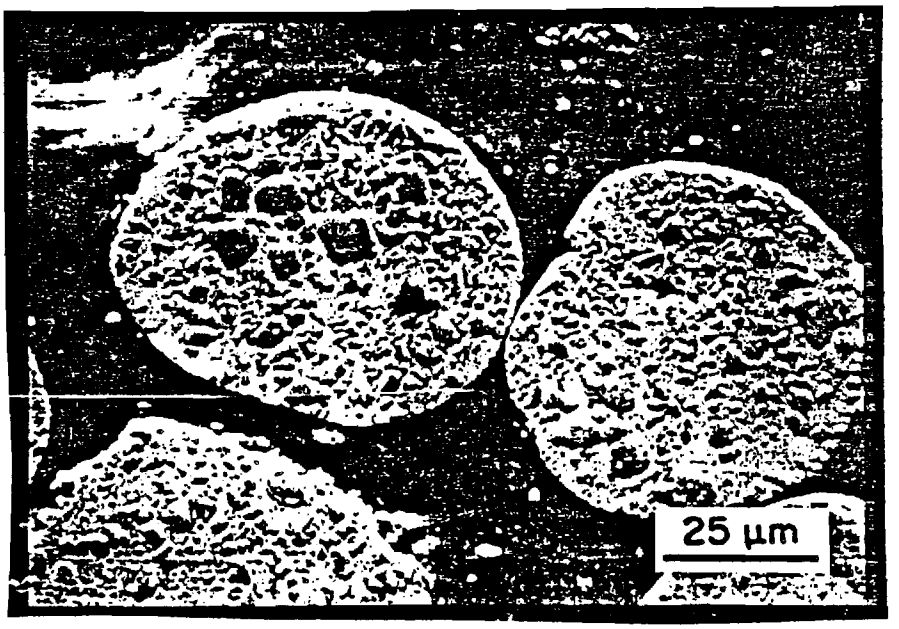


Fig. 1. Plasma melted Ni/Cr/TiC Particles

In the microatomization process, the molten agglomerates are impinging in a high velocity gas flow on a substrate where they breakup into a fine spherical powder. Figure 2 illustrates schematically the microatomization process. An example of microatomized powder out of -200 mesh copper particles is shown in Figure 3. Summarizing, the characteristics of the microatomization process are:

- It allows processing of a wide range of material compositions and melting temperatures.
- It yields powders with spherical morphology, smooth powder surfaces and few satellite particles.
- The microatomized powder yields range from 2% to 30%.
- The potential applications are seen in:

  (1) metal injection molding,

  (2) precision press and sinter parts,

  (3) precision HIP'd and forged parts, and

  (4) electronic components.

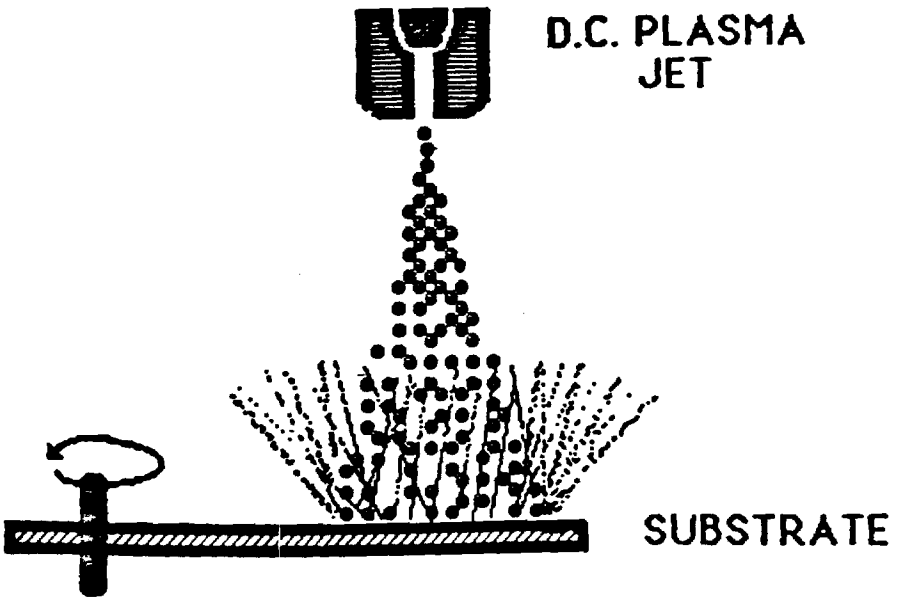


Fig. 2. Schematic of microatomization process.

ATOMIZED -200 MESH COPPER PLASMA MICROATOMIZED COPPER

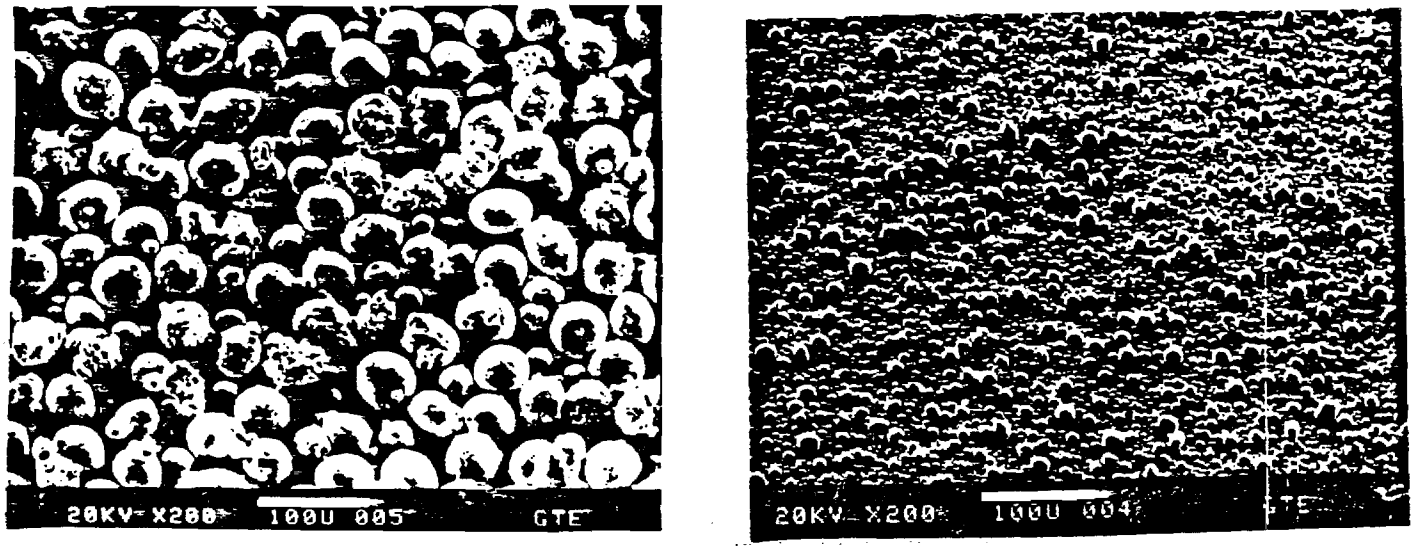


Fig. 3. Example of microatomized powder.

There are several commercial applications for the in-flight plasma process. Table I lists companies using this process and the associated products. The ZrO_2 generation from zircon has been a commercial process with a plasma torch specially developed for this purpose by Ionarc. Upon passing through the plasma, the zircon dissociates into separate ZrO_2 and SiO_2 phases which can be chemically separated. Yttria stabilized zirconia is being used by METCO for thermal barrier coatings. The particles are spherical with a smooth surface, but they are hollow. Table II shows the effect of the plasma densification process on Fe/Mo/C particles. A factor two in density can be gained by the plasma densification process.

Table I. Commercialized Use of In-Flight Plasma Processing of Materials

GTE Products Corporation	Various materials for thermal spray applications - WC/Co's, Mo, Cr_3C_2/Ni/Cr, TiC/Ni/Cr
	Ultra fine, pure, spherical specialty materials
METCO, Inc.	Hollow ZrO_2/Y_2O_3 particles for plasma sprayed thermal barrier coatings
Imperial Chemical Industries (formerly Transelco/Ferro formerly Ionarc)	ZrO_2 removed from plasma dissociated zircon
Plasma Materials, Inc. (now a Division of Norton)	Spherical magnetite for copier applications

TABLE II. Fe/Mo/C BULK DENSITIES (g/cc)

MESH	SPRAY DRIED AND SINTERED	PLASMA DENSIFIED
+200	1.74	3.19
-200+270	1.76	3.63
-270+325	1.81	3.63
-325+400	1.93	3.80
-400	--	4.06

Obviously, the process requires a match between starting powder size and plasma equipment in order to achieve melting of all particles. This is illustrated in Fig. 4 which shows the cross section of two types of plasma-melted pre-alloyed, chromium carbide, nickel, chromium particles. The particle indicated by the letter E shows coarse chromium carbide within the plasma melted nickel chromium matrix. The other spherical particles within the field of view have been totally plasma melted and the chromium carbide has been dissolved within the matrix and subsequently reprecipitated as an extremely fine dendritic second phase.

The disadvantages from a commercial point of view of the in-flight plasma process are:

- The plasma torch is a low-voltage high-current device which makes a DC power supply necessary.
- Torch power losses to the cooling water are usually more than 20%.

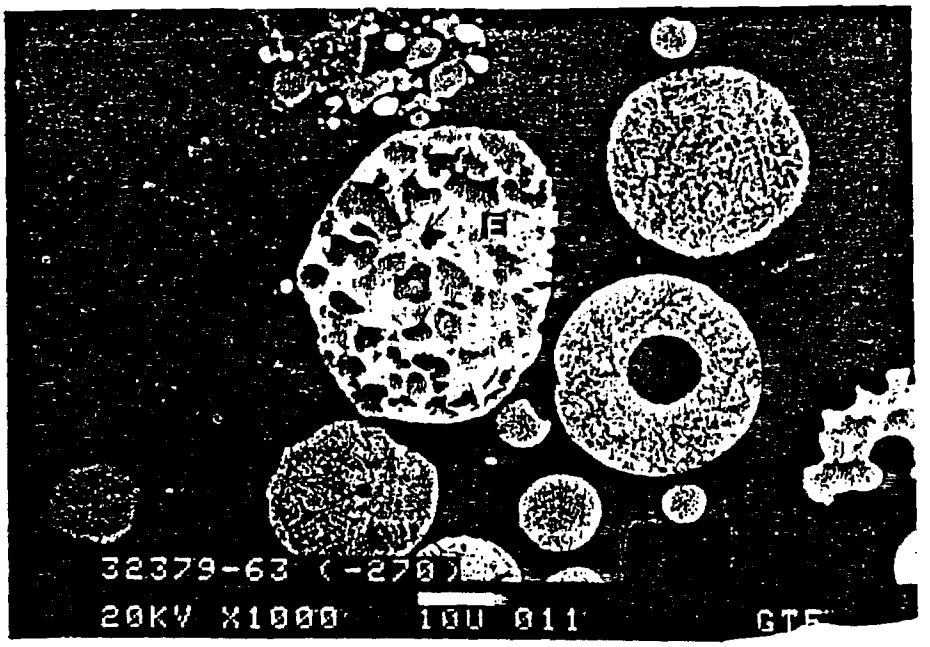


Fig. 4. Cross Sections of plasma melted particles.

- An inert gas is generally required to form the plasma, which may make the separation and recycling of the inert gas a necessity.
- Requirements for dispersed material feeds and plasma processing conditions are stringent.
- The efficiency of the in-flight heat transfer from plasma to particles is very low - a matter of 2-3% of the torch power - hence low throughput rates.
- Contaminations can be caused by electrode wear.
- The time-temperature histories of particles treated in a plasma jet are highly nonuniform.

The process controlling requirements for the in-flight plasma process are:

- Extended zone of plasma-particle interaction;
- Capability for an intensive and effective energy transfer to particles being processed;
- Minimal energy losses in the plasma-particle energy transfer zone;
- Large particles must be repeatedly affected by the plasma flow for full thermal treatment;
- Fast and effective quenching of dispersed materials;

There are a variety of approaches being pursued to achieve better control of the plasma for in-flight materials processing. Examples are:

- Extending the jet
  - high enthalpy, laminar plasma. Longer, hotter, low velocity flames allow for more efficient use of heat and longer dwell times.
  - Large particles (up to 0.015 in) can be processed but high feed rates may extinguish the torch.
  - Low pressure plasma deposition (LPPD) devices extend the length of the jet, have broader spray patterns, and yield clean deposits but at the expense of dwell time.

- Stretching the arc
  - Wall stabilized cascading arc technique
    * requires higher voltages, gives higher arc-to-gas heating efficiencies but material deposits on the wall result when introduction into the arc is attempted.
    * longer jets also result so external injection can be employed

- Transferred arc principle
  - two anodes at slightly different potentials

- Spinning/orbiting the plasma
  - potential for increasing the arc-to-gas and plasma-to-particle heating efficiency
  - magnetic arc rotation not as promising as hoped for but:
    * the anode heat load is evenly distributed and erosion is reduced
    * enthalpy level can be controlled by monitoring arc current and spinning velocity
    * relatively large volumes of gas can be heated to fairly uniform temperatures
    * rotation increased the potential drop so that more power can be delivered at a given current.

- combined spun plasma-stretched arc
  * arc-to-gas heating efficiencies as high as 80-90% have been achieved with this method.
  * USSR have produced 200mm plasma jet but still require monodispersed powdered materials.

- Modulation of plasma jet parameters

- Combining plasma devices may allow for the central feeding of powder to minimize trajectory variations, e.g.
  - Positioning similar jets in opposing fashion
  - Hybrid plasma reactors consisting of superposition of an rf plasma with an arc jet

Research which would advance the state of the art should be performed in the modeling and the equipment design areas. Specific recommendations for research are:

Modeling

- Interaction of arcs with magnetic and flow fields;
- Effects in the electrode regions and at the electrodes;
- Thermodynamic state of the arc plasmas (deviations from LTE);
- Plasma-surface interaction phenomena;
- Plasma-particle interaction under dense loading conditions.
- Predictions for those materials systems which will be successfully processable.

Equipment Design

- Reduce the high velocity, viscosity, and temperature gradients of a conventional linear plasma jet, thus allowing:
  - processing of a broad range of particle sizes
  - complete reaction/melting
- "higher" volume processing capability
- Improved feeding devices for all sizes of particles

5.2 MYSTERIES IN MAKING POWDERS

C. B. HOLDEN
Consultant
257 Church Street
Doylestown, OH 44230

Introduction

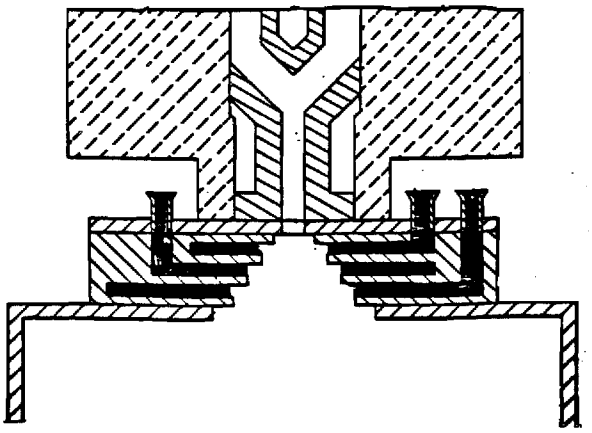
The mysteries presented here bedeviled 20 years of work at PPG Industries on plasma-heated processes making TiO_2, TiC, SiC, and TiB_2. These products are all produced as fine particles and are used as pigments or ceramic powders. For these applications, the particle characteristics must be optimized and then the process must be controlled to make the optimum product consistently. If the powder varies from batch to batch, it cannot be used because its behavior in the processing steps will vary.

It is easy to make the products. The trick is to define what is optimum and then to control all production to match those characteristics.

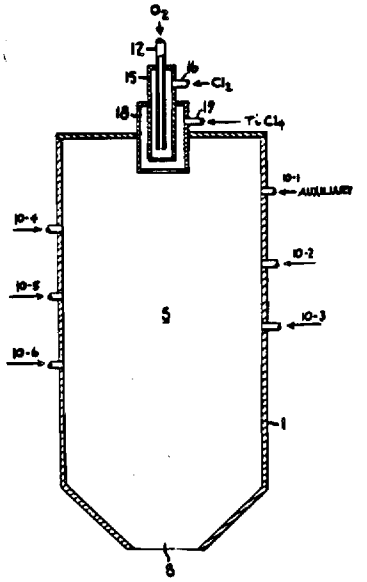
If these mysteries can be explained by future research it will reveal new tools for control of the product characteristics.

Background

The processes discussed here use vaporized raw materials rapidly mixed with a hot gas producing a cloud of solid particles suspended in the excess gas. Plasma is not necessary because all the ionized species are gone by the time of mixing. But plasma is a convenient way to heat the gas.

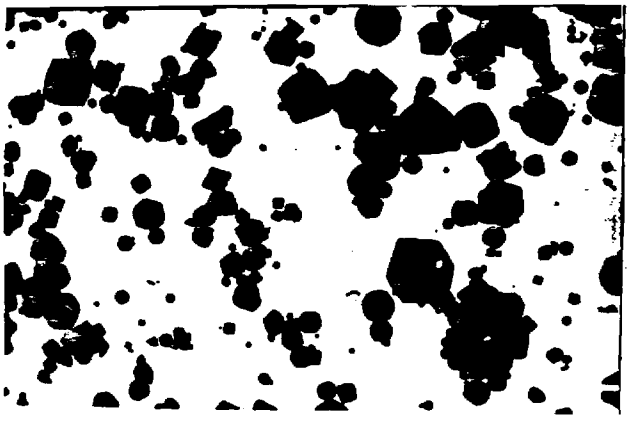


Typical Mixer Arrangement (US Pat. 3,761,576)

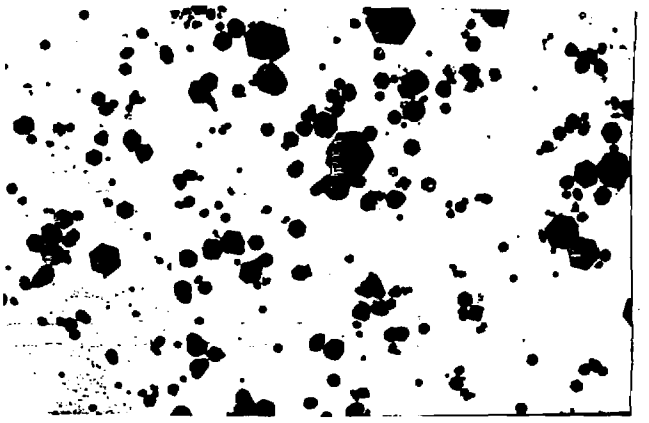


Typical Reactor Arrangement (US Pat.3,640,745)

Reactor holdup is 0.1 to 10 second and the flow patterns fit the description of a well-stirred reactor. Reaction temperatures are 1200 to 2000°C. The products are crystalline, mostly with well-developed faces and classical shapes such as hexagonal plates, tetragonal prisms, etc. Very few particles are sintered together into masses initially. However, powder which collects on surfaces in the reactor will become sintered and when it falls off and gets into the product it is called grit.



Typical TiC Powder



Typical TiB_2 Powder

Mysteries

1. How does nucleation occur in these processes? Can it be controlled and/or changed so as to control and/or change particle size?

   Because the powders are crystalline, classical nucleation theories should apply. The mystery is to understand exactly how this occurs in a turbulent gas stream with severe thermal and concentration gradients and within the short holdup time. The understanding needs to extend to ways to change particle size on command.

2. What are the nuclei in each case?

   In TiO_2, 1 to 3% of $SiCl_4$ and $AlCl_3$ were added to nucleate the TiO_2 particles. $AlCl_3$ oxidizes faster and then the Al_2O_3 serves to gather the Ti and O species onto its surface.

   In TiC, SiC and TiB_2 it never was clear just what made the nuclei.

3. How does turbulence in the mixing zone affect nucleation?

   Evidence indicates more intense mixing gives more nuclei as it does when solutions react to form crystalline products in an aqueous system. For example, when reacting sodium silicate with a dilute acid to form hydrous SiO_2, the more intense the mixing in the reaction zone, the smaller the particles (more nuclei).

4. How does the scale of operation affect nucleation and particle development?

   There has not been complete success in duplicating mixing parameters for scale-up. This makes the powder different when it is made in a larger reactor even though conditions were supposed to be the same.

5. How does the amount of internal recirculation in the reactor affect size distribution of the powder?

   It would appear that recirculation due to entrainment by the incoming jet of reactants would recycle particles formed previously and give them a chance to grow larger. Are larger particles simply some that have passed through the reaction zone more times?

6. Can mixing and reaction results in a turbulent regime be predicted from tests done with laminar flows? Also,

6a. What is the proper criterion for the turbulent-to-laminar transition in a mixer with 3 or 4 streams entering with different temperatures and directions?

   This is a scale-up problem which is faced when going to production scale.

7. What are the controlling reaction mechanisms in each reaction?

   These affect the reaction volumetric productivity. It appears relative productivity is SiC < TiC < TiB_2, but exactly why? Can anything be done to enhance the volumetric productivity?

8. What is the effect of momentary upsets in the feed ratio?

   This is the natural result of back-pressure fluctuations. Is it worthwhile to make extensive changes to overcome this problem?

9. How do reaction conditions define each of the characteristics of the powder? How is each one adjusted when it is necessary to change a characteristic? This is a mystery which summarizes and includes many of those stated previously.

   Characteristics which seem to be important and need to be controlled to keep the powder the same are:

   - Composition and impurities
   - Shape of particles
   - Median size of particles
   - Size distribution
   - Surface activity

   The last characteristic shows up as a different green density after compacting. Other measurements show the powders to be the same, but if this characteristic is different they do not compact to the same density.

10. What are the mechanisms of tungsten loss from the cathode of a hydrogen arc heater?

Many times the pattern and rate of tungsten loss seemed to change for no apparent reason. The reasons need to be identified so that good electrode life can be achieved consistently. Also, more information in this area may lead to improvement in the maximum size of arc heaters for commercial plants.

11. What instruments and control systems can best control a DC plasma arc heater to give a constant enthalpy in the exit gas? What instruments can be provided to give the operator a better feel of the operation?

12. What instruments and alarm systems can best detect trouble and assure prompt shutdown of a DC plasma arc heater? Should they respond to high amperage, extreme voltage swings, changing noise patterns, or others?

5.3 PLASMA CHEMICAL SYNTHESIS OF POWDERS

GERALD J. VOGT
Material Science and Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87545

Chemical synthesis within a thermal plasma is carried out by physically altering or chemically reacting injecting materials (gases, liquids, or solids). Complete vaporization or fragmentation with subsequent nucleation and growth after supersaturation produces submicron-sized powders of an altered or new species [1,2]. For example, the introduction of coarse nickel powder with a size distribution between 20 to 30 micron will yield a finer nickel powder with a reduced size range between 20 and 300 nm. Similarly, the reaction of $SiCl_4$, CH_4, and H_2 will yield beta-SiC with a controllable median size between 5 and 1000 nm.

The targeted powder properties generally sought for consolidation application typically include [3,4]:

- equiaxed morphology
- high chemical purity, especially at the surface
- median particle size between 20 and 100 nm or between 0.1 and 2 micron
- monomodal, narrow particle size distribution, or a bimodal distribution ($D_1/D_2 \sim 10$)
- no hard agglomeration

These powder characteristics are strongly desired for ceramic powders for the preparation of structural ceramics, but are generally not as important for ductile metal powders. While the need for these desired properties is not surprising, ceramists are still debating whether the optimum median size is greater or less than 0.1 micron. The question is whether particles of size less than 0.2 micron can be subsequently processed by colloidal techniques [4] to give green densities above 50% theoretical density. Moreover, ceramists are speculating that a bimodal or broader size distribution may be advantageous for green densities greater than the theoretical closest-packed density of 74% obtainable for monosized particles.

The potential application for plasma powders is perhaps the greatest in the area of structural ceramics. In ceramics, the goal is a pure ceramic with a lower sintering temperature and the absence of the conventional sintering aid, which is the major cause for high-temperature degradation of the ceramic properties. Just as important, greater control over ceramic processing and microstructure will hopefully improve reproducibility in the mechanical properties of finished ceramics, which has been a major and overriding problem for high performance ceramics [3]. For metals, potential benefits include finer microstructures, dispersion strengthening, and amorphous structures. In military applications, the potential gain is new lightweight and tougher armors and obscuration defenses. Future applications of noncompacted powders may include catalyst formation, catalyst substrates, and inorganic structural foams.

The current state-of-the-art in plasma chemical synthesis of powder is the empirical "black-box" application of the thermal plasma. Reactants are injected and powders are collected from the existing gas stream. As a direct result, the performance of the plasma reactor is solely judged by the powder properties

determined after synthesis. Invaluable insight to the plasma behavior is gained from current modeling and diagnostics [5], but the information is only qualitative. Quantitative information for particular process reactors is sorely needed for the practical improvement of process control and powder quality.

Some of the greatest research needs in plasma synthesis come from our incomplete understanding of plasma-solid particle interactions. In the injection of numerous particles or a large volume of gas, control of the reactant trajectory distribution is believed to be essential to insure uniform process conditions for uniform temperature histories and reaction histories of both reactants and product. Better understanding of heat, mass, and momentum transport is needed to control particle vaporization over short residence times ($<$1 ms) and to include the impact of reactant loading on plasma transport properties, thus insuring uniform temperature/reaction histories. Also, understanding of heterogeneous nucleation and growth within the plasma tail flame is needed to produce desired particle sizes and distributions. Moreover, the future application of ceramic powders is largely dependent on the ability to control particle agglomeration, especially "hard" agglomeration, which is typified by strong chemical bonding through material growth at contact points or by encapsulating films of a different phase.

Plasma synthesis also requires a better understanding of basic plasma fluid dynamics through modeling and diagnostics. The basic knowledge of cold-gas injection of carrier and reactant gases and the mixing of these cold gases with the hot plasma gas is fundamental to the control of uniform temperature/reaction histories. A critical aspect of cold-gas mixing with the plasma is cold-gas quenching of the plasma reactions. Quenching will most probably be the key to controlling heterogeneous particle growth and agglomeration, undesirable side reactions, and crystalline phase of the powder.

To facilitate modeling efforts to advance plasma synthesis control, a broader understanding of plasma reaction kinetics must be obtained. Currently, the experimental data base on pertinent reactions and their rate coefficients is fundamentally lacking for reactions between 1000 and 4000K [7]. Moreover, the necessary transport properties for gas mixtures are not available for use in plasma modeling [6].

Major developments in the plasma chemical synthesis of powders will require significant process and engineering improvements in such areas [6,7] as:

- practical modeling codes for the general design of plasma reactors that include the proper design criteria for reactant injection, quenching, and uniform processing conditions,

- reactor scale-up criteria for production reactor design from pilot or laboratory models,

- experimental studies on electrode wear in arc plasma reactors to provide longer electrode life and to lessen product contamination,

- a method to simply and rapidly measure rf-power coupled to induction plasma reactor,

- more efficient rf-generator designs for stable gas-plasma operation,
- reliable powder feeders for solid reactant injection with reproducible, constant feed and under controlled gas atmosphere,
- powder collection schemes for operation with hot gas streams and for collection and retrieval of air-sensitive powders under inert gas conditions,
- mass feed rate monitor for powder feeders, and
- real-time, in-situ process monitors conditions with rapid feedback of information on powder stoichiometry, particle size/agglomeration, and plasma enthalpy.

In summary, there is a great need for better understanding and control of plasma powder synthesis through model-assisted process design and diagnostic characterization of operating reactors. Toward this end, diagnostic verification of the modeling and the creation of a satisfactory data base for high-temperature kinetic and transport data must be pursued. The development of plasma powder synthesis requires experimental control of uniform processing histories for the ultimate control over powder stoichiometry and phase, particle size and distribution, particle agglomeration, and the synthesis of particle sizes greater than 0.1 micron.

References

1. R. M. Young and E. Pfender, "Generation and Behavior of Fine Particles in Thermal Plasmas--A Review," Plasma Chem. Plasma Process., 5(1) (1985) 1-37.

2. G. J. Vogt and L. R. Newkirk, "Thermal Plasma Synthesis of Powders," Proceedings of the Symposium on High Temperature Materials Chemistry-III, The Electrochemical Society, pp. 164-176 (1986).

3. H. Kent Bowen, "Basic Research Needs on High Temperature Ceramics for Energy Applications," Mater. Sci. Eng., 44(1) (1980) 1-56.

4. Proceedings of the 1986 Conference on Ceramic Powder Science and Technology, sponsored by the American Ceramics Society, Boston, MA, August 3-6, 1986. To be published as a volume in the "Advances in Ceramics" book series.

5. M. I. Boulos, "The Inductively Coupled R.F. (Radio Frequency) Plasma," Pure & Appl. Chem. 57(9) (1985) 1321-1352.

6. "Plasma Processing of Materials," Report NMAB-415, issued by the National Materials Advisory Board, National Research Council (1985).

7. J. V. R. Heberlein, "Research Needs in Arc Technology," Mat. Res. Soc. Symp. Proc., 30 (1984) 101-115.

5.4 RADIO-FREQUENCY THERMAL PLASMA SYNTHESIS

TOYONOBU YOSHIDA
Department of Metallurgy & Materials Science
University of Tokyo
Bunkyo, Tokyo, Japan

It has been said that the absence of electrodes, the large volume, and the moderate gas flow velocity make a radio-frequency(rf) plasma desirable for a variety of scientific and engineering applications. However, the absence of electrodes means that an rf plasma is very sensitive to external disturbances, such as an injection of reagents into the plasma. In fact, it has been often experienced that the injection of reagents results in turbulence and rapid quenching of an rf plasma when the amount of the reagents exceeds a certain relatively small quantity. It may fairly be said that this delicate character of an rf plasma has prevented the progress of rf plasma processings in various fields, though there has been increasing interest in the possibilities of an rf plasma for several industrial fields. Accordingly, the key to success for the operation of an rf plasma in various applications depends to a large extent upon the ability to sustain a stable plasma, in particular, when reagents are being injected in a power input region.

Based on the viewpoint mentioned above, we have developed two injection methods which overcome the shortcomings of the general configuration of an axial injection method. The first approach was the use of a radial injection method, in which the reagent was radially injected between turns of an induction coil. Effectiveness of this design was examined theoretically and experimentally, by applying it to the preparation of ultrafine alloy particles. The second approach was the use of the axial injection method in which the usual carrier gas flow was replaced by a plasma flow generated from a dc arc jet. The basic concept of this design is that if one uses an axial injection method, some auxiliary energy sources are needed to stabilize the rf plasma. We named this type of plasma "Hybrid Plasma". It should be pointed out that this hybrid plasma is different from the so-called combined plasma in a sense that the latter plasma is generated by the direct coupling of an rf electromagnetic field to a dc arc jet or dc arc column, while the hybrid plasma is rather characterized by the superposition of an rf plasma and an arc jet. The effectiveness of the hybrid plasma for the chemical synthesis was examined by applying it to the preparation of ultrafine silicon nitride and carbide particles. Though the validity of this torch design was confirmed to a considerable extent, extensive studies must be directed to the establishment of a more sophisticated one because the torch is the heart of this technology.

Before expecting the development of the rf plasma processes into the industrial scale, there are many other problems awaiting solution besides the torch design mentioned above, especially the following items:

1) control of an rf plasma flame, especially in the case of reagents injection,

2) control of the thermal histories and trajectories of the reactants,

3) control of the quenching processes, and

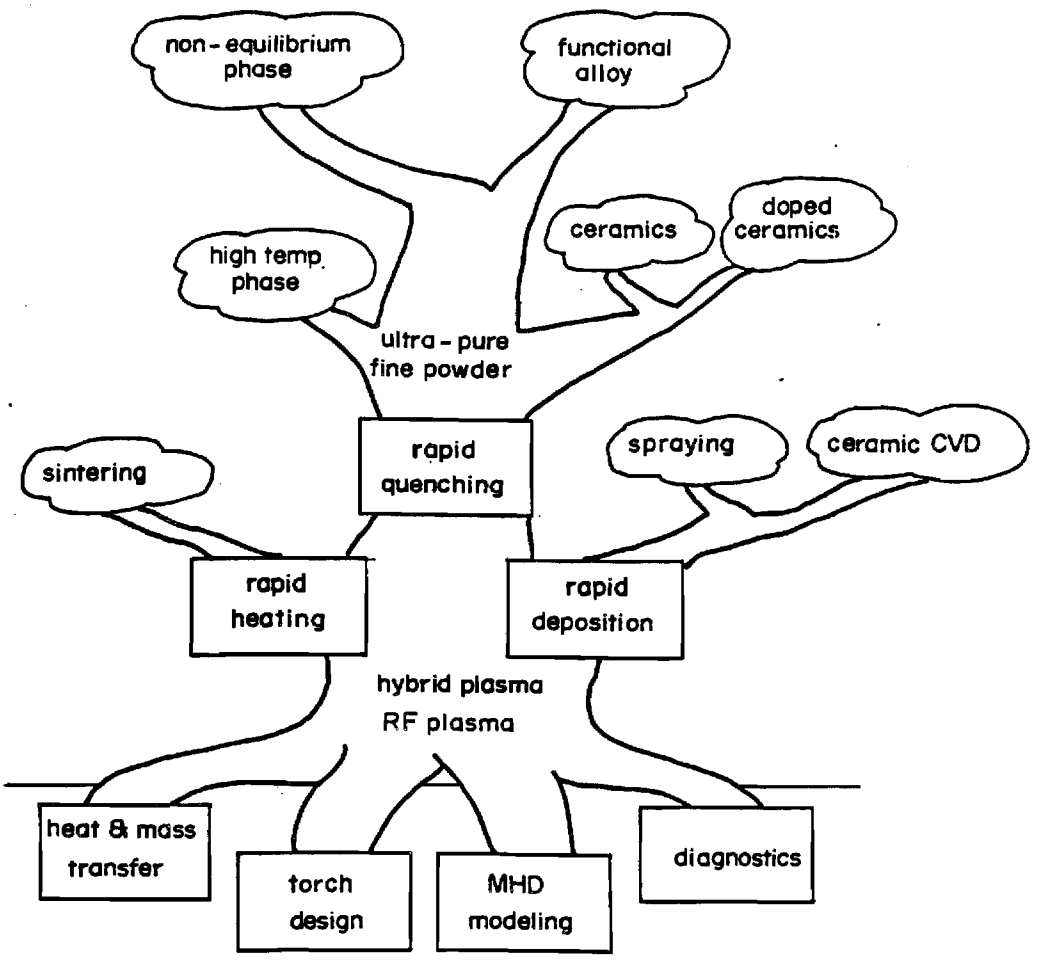
4) development of rf generators suited for multicomponent plasma generation with high efficiencies and high power.

A big national project has been started to solve the above mentioned problems sponsored by The Science and Technology Agency of Japan since the last year. Moreover, many Japanese enterprises have started studies for commercialization of rf plasma processes, especially in the fields of ceramics technology, by using a 100kW-level rf generator. Recently, a certain company developed a 100 kW-level hybrid plasma system and has successfully started using it for the formation of ultrafine ceramic powders. At this stage, the production rates of about the order of 10g/kW-h are reached in cases of nitrides and carbides formation. Judging from these circumstances, commercial processes are considered to be established in the very near future, though the cost of power in Japan is extremely high.

The following fields will be promising for the novel rf plasma processing, and must be studied for the bright future of this technology.

1) production of ultra-pure and fine ceramics
2) production of functional ultrafine alloy powders
3) production of special ultrafine powders with high temperature or nonequilibrium phases
4) ultra-high rate coating of ceramics by thermal plasma CVD
5) RF plasma spraying
6) RF plasma sintering

These subjects are now under study in our laboratory.



Promising fields for rf and hybrid plasma processing

THERMAL PLASMA TECHNOLOGY

CHAPTER 6

SYNTHESIS OF CHEMICALS

Session Chairman

T. N. Meyer
ALCOA Technical Center
Alcoa Center, Pennsylvania 15069

6.1 CHEMICAL PROCESSING WITH PLASMAS

R. J. MUNZ
Department of Chemical Engineering
McGill University
Montreal, Quebec, Canada H3A 2A7

Introduction

Thermal plasma processing can include almost any topic to be discussed at this workshop. Its definition for purposes of this contribution is more by elimination than by any universally accepted convention. Thermal plasma processing here includes hydrocarbon processing (acetylene manufacture, gas reforming, gasification of carbonaceous materials), the production of chemicals that are not addressed in extractive metallurgy or powder synthesis, and drying which is a physical process.

Opportunity Areas

Acetylene

The production of acetylene is a mature process which has been in operation at the Chemische Werke Huels for many years but outside of a brief application in the United States in the early 1970's has found no further application. The main reason for this is the economics of ethylene manufacture from liquid hydrocarbons which makes chemical synthesis of bulk chemicals via acetylene uneconomical. The only changes to the Huels process over the years have been using heavier and heavier feedstocks (gas to light liquid to heavy crude to coal).

A recent report on the potential of plasma technology applications in Canada [1] identified the thermal plasma production of acetylene for the manufacture of low volume specialty chemicals as an opportunity area. A techno-economic assessment based on the Huels process with natural gas as feed material showed that plants producing 50 million lb. of acetylene per year could produce acetylene at about $0.54/lb. compared to between $0.70 and $0.80/lb. using conventional methods. The cost differential between locating the plant in Alberta or Quebec was less than $0.02/lb.

The same report also examined the feasibility of producing acetylene at 300 million lb. per year, i.e. at the volume needed to produce bulk chemicals such as vinyl chloride monomer. Here the acetylene cost dropped to about $0.38/lb. which still cannot compete with ethylene at about $0.20/lb. Acetylene could command a premium of about $0.05/lb. over ethylene due to its desirability as a feedstock.

Finally, the feasibility of producing 12,500 barrels a day of gasoline from natural gas via plasma produced acetylene was examined for a plant located in Quebec. The process would have the advantage of replacing imported crude oil with readily available natural gas. Here the product cost ranged between $0.43 and $0.50/litre compared to the December 1985 cost of producing gasoline of $0.38/litre.

It appears that for acetylene production outside of the special case of Huels, only small scale production for specialty chemicals looks promising.

Gasification and Reforming

Gasification is the conversion of carbonaceous materials into gaseous products by reaction with air, steam, oxygen, or carbon dioxide. The products are usually a mixture of methane, hydrogen, and carbon oxides. The gas produced is usually destined for heating applications, but can also be used for synthesis after post treatment. The reactants may be coal, lignite, peat, wood, heavy crude and other similar materials.

Gas reforming is the reaction of light hydrocarbons with steam to form a mixture of methane, hydrogen, and carbon oxides. In this case, the product gas is usually used for chemical syntheses e.g. ammonia, methanol or as a reducing gas for pyrometallurgical operations.

Thermal plasmas can be used for both processes. In the direct reduction of iron ore the advantage of plasma reforming is that the process is relatively insensitive to the nature of the hydrocarbon feedstock [2]; the conventional industrial processes are catalytic and so are sensitive to catalyst poisoning in the presence of sulphur compounds. Plasma reforming also allows the substitution of electrical energy for chemical energy. Conventional processes usually burn part of the feedstock to drive the endothermic reactions.

In the steel industry, the application of plasma reforming must be closely integrated into the overall metallurgical process e.g. the SKF PLASMARED or PLASMASMELT processes; the waste heat produced is usually directly used in the metal reduction or pre-reduction and so the overall thermal efficiency can be quite high. The savings due to the application of plasma is primarily due to lower capital costs for the overall process. The biggest obstacle to the growth of plasma in this area is the poor financial health of the steel industry and the stagnant market for steel. Plasma process economics may be advantageous in new capacity or to reduce bottlenecks but cannot compete with fully amortized under-utilized conventional equipment.

A laboratory scale study of the gasification of peat in a steam plasma showed that high conversions are possible and that a gas which could be directly used to synthesize methanol can be produced [3]. The use of the steam gasification process operating at methanol synthesis pressures could reduce the overall process cost since the need for synthesis gas compression would be eliminated. The major economic concern here is the fluctuating price and demand for methanol.

A recent report [4] concluded that the plasma pyrolysis of wood to produce heating gas was uneconomical.

Another interesting application of steam or hydrogen plasmas is in the upgrading of heavy oil. Much of North American oil reserves are in the form of very heavy crudes or residues to which hydrogen must be added or from which carbon must be rejected to form transportation fuels. The use of a steam plasma can in principal carry out both reactions and has recently been investigated [5]. Although the conversion to gas could be easily controlled and good production of acetylene was obtained, no light liquid hydrocarbons, which are predicted to form at high temperatures and very short residence times, were isolated in this study. The results obtained suggested that more fundamental work on the kinetics of this complex system is needed so that the selectivity of reaction can be enhanced by optimum choice of operating conditions. Although there is a present glut of conventional oil at low prices, the processing of heavy oils will once again become very important to North American economics.

Drying

The use of superheated steam as a fluid for drying is receiving a great deal of interest at present. The main advantages of the process is that the latent heat of vaporization can be recovered at low capital cost and product deterioration is much less than with air at similar temperatures. Hazards of combustion or explosion are also eliminated. The potential advantage of using plasma-heated steam as the energy source for this type of drying is the high capital cost for both the dryer and the steam heating system. A large and rather expensive superheater might be replaced by a plasma torch or set of torches. Because of the very high enthalpy of steam at plasma temperatures, relatively low flow rates need actually pass through the plasma torch. The potential application areas would be in mineral drying where a high temperature can be tolerated and the product contains little internal moisture. Gauvin [6] has examined the use of plasma torches in spray dryers and found the results very promising. Rather little work has been done in this area as yet due to the difficulty of using pure steam as a plasma gas.

Treatment of Toxic Wastes

Thermal plasmas represent an ideal solution to the destruction of organic toxic materials such as polychlorinated biphenyls which can only be rendered harmless by incineration at very high temperatures. A number of reactor systems have been developed for this purpose but their design and operation could certainly be improved by more research.

Black Liquor Treatment

A major processing problem in the pulp and paper industry is the recovery of sodium sulphide and sodium hydroxide from black liquor which is a mixture of lignin, depleted sodium chemical. The process is presently carried out in a Tomlinson furnace which is costly and hazardous. SKF have examined the use of a plasma gasification process for black liquor at a capacity of 0.5 ton/h [7,8]. A problem to date has been the formation of sodium carbonate rather than sodium hydroxide; this is due to insufficient quench and over-oxidation. Work on a similar process is underway at McGill University; here the work is aimed at eliminating sodium carbonate formation.

Phosphorous

There is considerable interest in the Soviet Union in the plasma production of phosphorous based fertilizers from phosphate rock using plasma treatment [9].

Problem Areas

A major problem area in thermal plasma chemical processing is lack of reaction selectivity. As long as the reactants and products are both very simple (as in the case of acetylene production from methane for example), good conversions and yields can be achieved. Once the reactants become heterogeneous and complex products are desired, plasma reactors in their present state of development become much less useful. A great variety of products and by-products are normally produced and the cost of separation processes may exceed that of the plasma process. A lack of fundamental data on the thermodynamics and kinetics of the reactions involved in complex systems makes the analysis of experimental results frustrating and scale-up very difficult.

If the reactants are condensed phase, the injection of these into a suitable reaction zone can be very difficult. Liquid atomization can produce a wide particle size distribution which when combined with steep thermal gradients in the reactor, results in widely differing reaction histories.

Another problem area is that of electrode erosion in plasma devices. At present, electrodes must be changed about every 250 hours. In many systems, the separation equipment may take many hours to reach equilibrium and so even very short down times can be very detrimental. Many opportunity areas involve the use of a steam plasma on which practically no erosion rate data are available.

Important Research Problems

1. Kinetic studies of fast high temperature reactions
   - heterogeneous systems are certain to be at nonequilibrium both during the reaction phase and during the quench phase
   - data are needed at very short reaction times (ms time scale) in moderately complex systems
   - fluid dynamics studies of various plasma reactor geometries
   - temperature profiles in plasma reactors

2. Development of steam plasma torches
   - characterization, electrode erosion, stability

Diagnostic Tools

Needed Information

Independent measurement of gas and condensed phase temperature, velocity, and chemical composition in dirty and complex systems both with high temporal and spatial resolution.

References

1. Mikhlin, J.A., "Survey of the potential of plasma technology application in Canada" Final report by the Technical Development Department of SNC Inc. to CANMET, Energy Mines and Resources Canada, DDS File number 26SQ.23440-4-9010 November 1985.

2. M. G. Drouet, "Plasma Technology: Review of the state of the art and its potential in Canada" Report prepared for the Canadian Electrical Association CEA Report 126 U 322, March 1984, Chapter 2, Application of plasma technology in the Canadian iron and steel industry.

3. Stuart, P.R., R. J. Munz, and W. H. Gauvin, "Synthesis gas production from peat using a steam plasma," Plasma Chemistry and Plasma Processing Vol. 4, No. 4, 297-313, 1984.

4. Simonsen, H. I., "Economic feasibility of wood gasification using a plasma pyrolysis reactor" PAPRICAN report for Energy Mines and Resources Canada, March 1985.

5. Kubanek, G. J., R. J. Munz, and W. H. Gauvin, "Heavy oil processing in steam and hydrogen plasmas," Canadian J. Chem. Engineering, October 1986.

6. Gauvin, W. H., in ref. 1, Chapter 7, Application of plasma technology to drying operations.

7. Chemical Engineering, Vol. 93, No. 6, p. 19, March 31, 1986.

8. Bernard, R., and S. Kopparberg, "Plasma gasification of Kraft thick liquor" TAPPI proceedings, 1985 International Chemical Recovery, pp. 245-247.

9. Moss, A. L. et al., "Production of condensed phosphate by plasma chemical treatment of phosphate raw material" Plasma Chemistry and Plasma Processing, Vol. 5, No. 3, pp. 275-282 (1985).

THERMAL PLASMA RESEARCH AREAS

CHAPTER 7

DIAGNOSTICS

Session Chairman

S. A. Self
Mechanical Engineering Department
Stanford University
Stanford, California 94305

7.1 SURVEY OF DIAGNOSTIC METHODS

S. A. SELF
Mechanical Engineering Department
Stanford University
Stanford, California 94305

A number of review articles and references are available which present additional detail about the diagnostic methods discussed here [1-7]. Many of the techniques developed for combustion and MHD diagnostics are relevant to low temperature thermal plasma processing, both with and without particulates.

Classification of Diagnostic Techniques

Diagnostic measurements can be made by intrusive methods that perturb the plasma or non-intrusive methods that are external and non-perturbing.

The intrusive methods involve material probes for localized measurements. In situ techniques include thermocouple, pitot, enthalpy, fiber optic, Langmuir, conductivity, particle collection, and electric or magnetic field strength probes. Ex-situ techniques route the sample into on-line or off-line instruments, such as mass spectrometers, gas chromatographs, particle analyzers and microscopes or use some other microanalytical techniques (for particles).

The nonintrusive methods usually employ electromagnetic radiation or (rarely) particles. Passive techniques are based on emitted radiation. Active techniques may use radiation probes, particle beam probes, or tracer addition. Radiation probes may have either an incoherent (lamp) or a coherent (laser) source, measuring transmission (via interferometry, Schlieren systems, shadowgraph or holography); absorption or extinction (via atomic or molecular spectroscopy or particle extinction); and elastic (Thomson, Rayleigh or Mie) or inelastic (Raman, CARS, laser induced fluorescence, etc.) scattering. Note that many optical methods are impaired by the presence of particulates and fail when the optical depth is large due to particle absorption or scattering.

Characteristics of Diagnostic Techniques

The radiation methods cover the spectrum from the μ-wave to the ultraviolet. The signal to noise ratio depends on the following.

- Time resolution based on the data rate, bandwidth, and measurement time which can be improved using coherent detection with lock-in, boxcar techniques.
- Space resolution based on imaging or nonimaging optics using either line of sight averaging (with inversion or tomography) or 3-D (point) resolved techniques.
- Spectral resolution using monochromators, Fabry-Perot interferometers, or filters in the scanning, polychromator or optical multichannel analyzer (OMA) modes.
- The sensitivity, absolute accuracy, and dynamic range of the instrumentation.
- The noise level in the form of thermal (Johnson), shot (photon), electronic (i/f), etc.

The evaluation methods may be direct (based on a simple and well-validated theory)

or indirect (based on a complex model or other data needed to interpret the signal). Calibration may be absolute to determine actual densities, etc. or relative to determine mole fractions or population temperatures.

The robustness of the instrumentation is important to assure reliability under repeated measurement and over long periods of time, as well as immunity to interference. One must consider the proposed site. Is the experiment to be performed in a small scale, laboratory environment or in the field with a large rig and in a hostile environment?

Consideration of manual, semiautomatic or automatic measurements must be considered carefully. Are the measurements to be part of a standard laboratory procedure and applied to successive experiments? Is computer control of the experiment necessary or just convenient? Should a computer be interfaced with the experiment for data acquisition, reduction, display and/or recording of data? Will the benefits justify the additional cost in dollars and effort? Cost effectiveness must also extend to the maintenance costs including expert manhours required (e.g. for CARS spectroscopy) as applied to sophisticated versus simple experiments.

Parameters of Interest

Table I indicates various general parameters of interest along with specific measurable variables. The general parameters include gas velocity, gas temperature, enthalpy, refractive index, neutral and charged species concentrations, electric and magnetic field strengths, electrical conductivity, and information about macroscopic particles.

Gas Velocity (vector)

Pitot tubes (water cooled) can be used to measure mean velocity, $\bar{u}$, in uniform flow at values larger than one m/s. Optical methods can also be used for $\bar{u}$ with passive or active techniques when the spectral lines are weakly broadened. Passive techniques include luminosity fluctuations via a two-point correlation or line emission via Doppler shift measurements at two angles. Both are line of sight measurements. Active techniques are also Doppler shift measurements including the line of sight, line absorption technique or the point measurement of fluorescence, Rayleigh scattering or Mie scattering.

Mie scattering involves tracer particles of 1 micron or less made from refractory materials. Laser doppler anemometers (LDA) using crossed beam (fringe or heterodyne) methods can be used to make point measurement of $\bar{u}$, $\bar{v}$, $\bar{w}$, u, v, and f(u) to 500 m/s. In addition, if $\bar{u}/c_{sound} \geq 1$, then LDA single beam (optical shift) and two-beam transit time methods can determine $\bar{u}$ and $f(\bar{u})$. Finally, imaging-flow visualization methods can obtain the velocity from the length of track on successive exposures from spark photography, holography, a laser sheet beam, etc.

Gas Temperature and Enthalpy

The following discussion assumes that the plasma is in local thermodynamic equilibrium.

Probes can be used for local measurements in the transient mode or, if cooled, in the steady state mode.

Table I. Parameters of Interest

General	Specific
1. Gas Velocity (vector)	$\bar{u}$, u (turbulence) Flow pattern
2. Gas Temperature	
In Equilibrium	T
In Nonequilibrium	$T_e, T_+, T_-, T_{rot}, T_{vibr}, T_{ex}$
3. Enthalpy	Total enthalpy
4. Refractive Index	Bound electrons - composition, density Free electrons
5. Neutral Species Concentrations	Major and minor species, n_n Excited state populations Radicals
6. Charged Species Concentrations	n_e, n_+, n_i (ion type)
7. Electric, Magnetic Fields	E, H (vectors)
8. Electrical Conductivity	σ
9. Macroscopic Particulates	Mass loading, Γ_m
Clusters (100Å)or rocks(1mm)	Size distribution, f(d)
Morphology	Velocity, $u_p(d)$
Composition	Temperature, $T_p(d)$
Phase, etc.	

- Thermocouples (Ir/Ir-Rh) can be used to 2400K. Corrections for radiative and catalytic effects must be made.
- Heat transfer probes can be used to measure ΔT through a known thermal resistance.
- Fiber-optic probes can be used on optically dense lines with an appropriate filter and photo diode. Calibration can be made with a tungsten filament lamp to 3000 K. Response times can be on the order of one ms.
- Enthalpy probes can measure total enthalpy via calorimetric methods. Proper isokinetic design is required, hence, the probes can also be used as a gaseous sampling probe for composition.

Optical methods for temperature include the passive, line of sight, measurement of optically thin spectral lines to obtain relative or absolute line and/or continuum emission, emission coefficients. Temperatures can then be obtained from [3-6]

- two or more neutral line ratio method or Boltzmann plots.
- ion-neutral two-line ratio method.
- neutral line-continuum ratio method.
- absolute line or continuum emission coefficients.

Active optical techniques involve absorption/emission line of sight

measurements of spectral lines or the wings of optically thick lines (which are independent of α_λ). Conventional line reversal methods are manual, slow, and limited to the temperature of the source lamp whose radiation is being absorbed by the gas. With tungsten filament lamps traceable to the International Temperature Scale via NBS calibration the limits are 3000 K ($\pm$ 20° K). Temperatures higher than the maximum lamp temperature can be measured using the generalized line reversal method. Automated, fiber optic, fast instrument (1 ms) packages have been designed which also include corrections for particle scattering [8].

Refractive Index

Measurements of the refractive index of a plasma can yield the free-electron density or bound-electron composition and density. The complex refractive index, a function of wavelength, $m = m(\lambda)$, is composed of a real and an imaginary component, $m = (n - in')$, where n' is due to the effect of absorption. If one looks remote from absorption lines then

$$m(\lambda) = 1 + \sum_s C_s(\lambda) n_s - (f_p^2/2)/[f(f-i\nu)], \qquad (1)$$

where the middle term on the rhs is from bound electrons and the last is from free electrons. C_s depends on the species, s, and the summation represents integration over the line of sight. Also ν is the elastic collision frequency between electrons and neutrals, i is the imaginary number, $f_p = (1/2\pi)\,(n_e e^2/\epsilon_0 m_e)^{1/2}$ is the plasma frequency, and the working frequency, $f > f_p$.

In the visible spectrum, the free-electron contribution is often negligible. Imaging techniques can be used for flow visualization of mixing flows or for gas density (which is proportional to 1/T for homogeneous gases at constant p). Techniques often used are:

- laser or holographic interferometry.
- Schlieren, Shadowgraph or Moire fringes with white or laser light.

In the far infrared spectrum, the free-electron contribution is dominant. Single beam methods are usually used. Absolute methods for n_e are unaffected by particulates if $\lambda > d_p$. Techniques often used are:

- Laser interferometry.
- Michelson, Fabry-Perot, Mach-Zehnder interferometry.
- Faraday rotation in a strong magnetic field [10].

Neutral Species Concentrations

Methods for determining major species, excited state population and radical concentrations may be via probes or optical methods. In-situ, local measurements can be made with fiber-optic probes detecting ultraviolet, visible or infrared line absorption. Ex-situ, local samples can be analyzed by a remote mass spectrometer, gas chromatograph, etc.

Optically, passive line of sight, spectral line emission coefficient determinations via absolute intensities can yield excited-level densities and equilibrium concentrations. Active measurements of line absorption from the ultraviolet to the infrared using a tunable laser can yield similar results. Point measurements can be made with a tunable laser via fluorescence (in the ultraviolet and visible) or via scattering (Rayleigh, Raman or CARS). The tunable laser can also be used with imaging fluorescence (sheet beam) techniques for the visualization of mixing, reacting flows.

All the above methods require absolute intensity measurements. Calibration problems exist for excited states and radicals. Fluorescence measurements experience quenching problems.

Charged Particle Concentrations and Electrical Conductivity

The charged particle concentrations to be determined are the electron density, n_e, the positive ion n_+, and the negative ion n_-. The electrical conductivity is given by

$$\sigma = e\,(\mu_e n_e + \mu_+ n_+ + \mu_- n_-) \simeq e\,\mu_e n_e. \tag{2}$$

Probe methods [7] require a short exposure time and hence a good time response (10 kHz). Spherical or cylindrical Langmuir (electric) probes can be used to measure n_+ using the Clement-Smy theory for a collision dominated, flowing plasma. The n_e can be determined with a four-wire or RF conductivity probe (with Q-reduction). The electron mobility, μ_e, is a weak function of the gas and the temperature and is usually calculable.

Optical methods for n_e include passive, line of sight, freebound continuum emission coefficients (absolute intensity) when $n_e > 10^{12}$ cm^{-3} or Stark broadened line width when $n_e > 10^{15}$ cm^{-3}. Active, line of sight absorption measurements of Stark broadened line width can be made with a tunable laser. Point measurements of n_e can be determined similarly with laser induced fluorescence. In the far infrared, line of sight laser interferometric measurements of the refractive index can be made to obtain accurate and precise n_e, even in nonequilibrium plasmas.

The positive ion density (as well as n_e) can be obtained using line absorption techniques [9]. The negative ion density can also be obtained using line absorption if suitable bound levels are available. The absorption is due to photo-detachment.

Particulates

Macroscopic particulates may range from 100 Å to 1 mm rocks (5 orders of magnitude). Of interest is the mass flux Γ_m, particulate velocity u_p, mean size $\bar{d}$, size distribution f(d), and particulate temperature T_p.

Probes can be used to measure the total mass flux via isokinetic flows and filters of porous stainless steel (0.5 μm pores) with off-line weighing and other analyses. Particulate sampling filters using isokinetic impaction on fine Ir wire can be used with off-line SEM for size analysis of droplets ($d > 0.3$ μm). Isokinetic sampling and quenching the particulate flow prior to an on line particle sizing instrument can yield size distributions from 0.3 to 10 μm with an optical counter or from 0.01 to 1.0 μm with an electronic aerosol analyzer.

Most optical methods have a limited dynamic range for size, velocity and loading. Particles outside the range may interfere with reliable measurements within the range.

Particulate velocity point measurements can be obtained via crossed-beam, laser-Doppler anemometry or the two-beam transit timing techniques. Imaging methods for flow visualization include the (pulsed) sheet-laser beam, photography (u_p from track length or multiple exposure) or 3-D laser holography.

Particulate size distributions f(d) can be obtained from laser forward scattering [11] (1-50 μm) or laser two-angle scattering techniques. Two-wavelength laser extinction [12] for high velocity can determine $0.3 < \bar{d} < 3.5$ μm. Diffusion broadening of laser spectroscopy is useful in the range $0.003 < \bar{d} < 1$ μm.

Particulate temperatures can be obtained via 2-λ pyrometry in optically thin regions. The measurement is triggered when the particulate scatters the laser beam. This method can also be used for size and velocity [2].

References

1. S. A. Self and C. H. Kruger, "Diagnostic methods in combustion MHD flows," AIAA Paper 76-310 (1976) or J. Energy, 1 (1) 25-43 (1977).

2. M. Boulos, P. Fauchais and E. Pfender, Diagnostic Techniques in Thermal Plasma Processing, Parts I & II, DOE/ER-0270, vol. 1 & 2, NTIS, U.S. Dept. of Commerce, Springfield, VA (1986). Contains 438 references.

3. H. R. Griem, Plasma Spectroscopy, McGraw Hill, New York (1964).

4. R. H. Huddlestone and S. L. Leonard, (Eds.) Plasma Diagnostic Techniques, Academic Press, New York (1965).

5. W. Lochte-Holtgreven (Ed.), Plasma Diagnostics, North Holland Publ. Co., Amsterdam (1968).

6. T. L. Eddy, "Critical review of plasma spectroscopic diagnostics via MTE," IEEE Trans. Plasma Science, PS-4 (2), 103-111 (1976).

7. P. R. Smy, "The use of Langmuir probes in the study of high pressure plasmas," Advances in Physics, 25 (5) 517-553 (1976).

8. P. H. Paul, Spectroradiometric Temperature Measurements in Two-Phase Combustion Plasmas, HTGDL Rept. No. T-238, Stanford University, May (1984).

9. K. D. Annen, P. J. Kuzmenko, R. L. Keating and S. A. Self, "Electron and positive ion measurements in MHD combustion plasmas with phosphorous addition," J. Energy, 5, 31-38 (1981).

10. P. J. Kuzmenko and S. A. Self, "Measurement of plasma conductivity using Faraday rotation of sub-millimeter waves," J. Energy, 7, 176-181 (1983).

11. D. Holve and S. A. Self, Applied Optics, 18, 1632 (1979) and 18, 1646 (1979).

12. P. C. Ariessohn, S. A. Self and R. H. Eustis, "Two-wavelength laser transmissometer for measurement of mean size and concentration of coal ash droplets," Appl. Optics, 19, 3775-3781 (1980).

7.2 NON-LTE DIAGNOSTICS VIA EMISSION SPECTROSCOPY

T. L. EDDY
Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

When doing emission spectroscopy, one must separate that which is known, directly measurable or directly calculable from that which depends upon assumptions of a particular thermodynamic model.

Known Variables

Let us consider the simple case of a wall-stabilized arc with an atomic plasma. If the current density is not extreme, secondary ionization will not occur and quasineutrality gives

$$N_e = N_i. \tag{1}$$

If absolute spectral line (net) intensities, $I_L(x)$, are laterally measured, with corrections for absorption [1-3] when necessary, the Abel transform [4a] can be applied to circular cross sections, or asymmetrical methods [5-7] to noncircular cross sections, or division by length methods [8] for uniform lines of sight ($i_L = I(x)/\ell$) to obtain local line emission coefficients, $i_L(r)$. The $i_L(r)$ is related to the density of the emitting level, N_m, via

$$i_L = (hc/4\pi\lambda)A_{mn}\, N_m \tag{2}$$

where A_{mn} is the atomic transition probability between energy levels m and n and usually has an uncertainty (10-50%) which is larger than the error of measurement (5-10%). Nevertheless, we can determine a number of N_m from an equivalent number of appropriately chosen i_L. These are usually high lying levels and are usually found to approach a straight line on a Boltzmann plot as $m \to \infty$ (see Fig. 1). The straight line has a slope of $-1/T_{ex\beta}$ as defined for levels $m > m'$ via the Boltzmann factors [9]:

$$N_m/N_n = (g_m/g_n)\, \exp\left[\frac{-(E_m-E_n)}{kT_{ex\beta}}\right] \tag{3}$$

We can also determine a convenient reference point at the ionization limit, N_∞/g_∞ (or N_I/g_I if the lowered ionization level is used) [9,10]:

$$N_\infty/g_\infty = (N_m/g_m)\exp[-(E_\infty-E_m)/kT_{ex\beta}] \tag{4}$$

The radial electron density, $N_e(r)$ can be determined, via Stark broadening. The Stark broadening theory can be calibrated to the LTE independent 2-λ interferometrically obtained N_e [8],

$$N_e = C_\lambda\, N_{e,\ \text{Stark}} \tag{5}$$

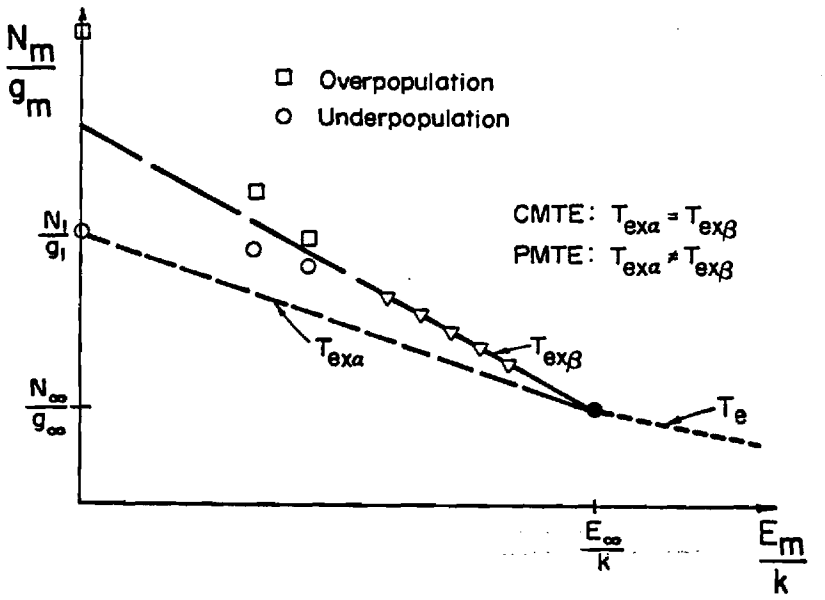


Fig. 1. Meaningful plasma temperatures:
- T_e ~ free electron translational temperature.
- T_g ~ atom, ion, or gas translational temperature.
- $T_{ex\beta}$ ~ upper level electronic excitation temperature.
- T_{exa} ~ total electronic excitation or Boltzmann temperature between m = 1 and m = ∞.

where $C_\lambda = 1.15$ for the Griem, Kolb, Shen theory [11] and $C_\lambda = 1.087$ for the Vidal, Cooper, Smith theory [12].

The known variables are then $T_{ex\beta}$, N_∞/g_∞ and N_e, as well as the measured N_m. Still needed are N_a, T_e, T_g and the departure coefficients b_m or the equivalent level population temperatures, T_{exm} (between the ground state and excited level m), to determine the thermodynamic state of the plasma.

Model Equations for Solution

Equations available are the Boltzmann factors to the ground state [9],

$$N_\infty/g_\infty = (N_1/g_1)\exp[-E_\infty/kT_{exa}) \tag{6}$$

$$= (N_a/Z_{exa})\exp(-E_\infty/kT_{exa}) \ , \tag{7}$$

which defines and introduces another variable, the total excitation or ground state ionization temperature, T_{exa}, between N_1 and N_∞; the equation of state,

$$p = N_a kT_g + N_e k(T_g+T_e); \tag{8}$$

and an appropriate ionization equation based on the model to be assumed. Here we will use generalized multi-thermal equilibrium (GMTE) [13,14] which can be reduced to or expressed equivalent to LTE, 2-T, PLTE, Collisional-Radiative, and MTE models. The GMTE total ionization equation is

$$N_e\left[\frac{N_i}{N_a}\right]^{T_g/T_e} = 2\left[\frac{Z_{exi}}{Z_{exa}}\right]^{T_{exa}/T_e}\left[\frac{2\pi m_e kT_e}{h^2}\right]^{3/2}\exp\left[\frac{-E_\infty}{kT_e}\right], \qquad (9A)$$

and the GMTE upper level ionization equation extended to the ionization limit ($m\to\infty$) is

$$N_e\left[\frac{N_i}{N_\infty}\right]^{T_g/T_e} = 2\left[\frac{Z_{exa}}{g_\infty}\right]^{T_g/T_e}\left[\frac{Z_{exi}}{Z_{exa}}\right]^{T_{exa}/T_e}\left[\frac{2\pi m_e kT_e}{h^2}\right]^{3/2}$$

$$\cdot \exp\left[\frac{-E_I}{kT_e}\left(1-\frac{T_g}{T_{exa}}\right)\right]. \qquad (9B)$$

where it is assumed that $T_{exa} = T_{exi}$.

Since (9A) and (9B) are equivalent, one more equation is needed to solve for N_a, T_g, T_e and T_{exa}. Possibilities include the free-free contribution to the continuum radiation [14, 16], various "direct" measurements of T_g [17-23], using the Low-T assumption that $T_{exa} \sim T_{LTE}$ [24], or obtaining T_e/T_g from electric field strength measurements [17-19, 25]. Each of these methods is relatively limited.

- The Low-T method ($T \ll T_{exa,\ normal}$) is the easiest to apply and holds in arcs and jets of smaller degrees of ionization. T_{LTE} is calculated from i_L of an upper level. Since $T_{exa} \simeq T_{LTE}$, (7) gives N_a so that (8) and (9B) can be solved simultaneously.

- If the local field strength E is known, T_e/T_g can be estimated from [25]

$$\frac{T_e - T_g}{T_e} = \frac{\pi}{24}\,\frac{m_e}{m_h}\left[\frac{\lambda_e E e}{kT_e}\right]^2. \qquad (10)$$

where λ_e is the electron mean free path. Equation (10) does not appear to be applicable when there is cold gas/particulate injection or when in the plasma boundary regions [24], because of the difficulty in determining the local E value, transient, and diffusion effects. In the latter case, the electron-energy equation including conduction, convection and diffusion effects must be used [17-19]. If (10) or the equivalent from [17-19] is usable, then (7), (8), (9B) and (10) result in a solution.

• Direct determination of T_e from excited level populations has been shown to be invalid in general [10]. It appears that one of the few reliable, but limited ways to obtain T_e is from probe measurements [15]. The free-free continuum can also be used to determine T_e when T_e is large or in spectral regions where the free-bound continuum relinquishes its dominance [14,16, 26,27]. The form of the continuum equation is not firmly established, but should reflect multitemperature or collisional-radiative parameters.

• Direct measurements of T_g include the short circuit method [17-19], for which PLTE is assumed and is applied at low currents in atmospheric arcs. At time zero, the arc is short circuited, which results in a sudden rise in the line emission coefficient, then a slower decay. The first change is attributed to equilibration of electron and atom translational energies, the second is due to recombination. The upper level ionization equation and line emission coefficients are used to relate T_e, measured before the jump to $T_g = T_{e,2}$ after the jump assuming that the electron density is constant.

• Doppler broadening measurements can also be used to determine T_g directly [4b,22]. The unfolding of the Doppler profile can be enhanced by a high resolution Dye laser which excites a narrow wavelength of the line and utilizes the emission to determine the Doppler width with multiple applications.

• T_g can also be determined from the rotational contribution to the vibrational/electronic bands of diatomic molecules such as nitrogen and hydrogen. The application is limited to lower temperatures, i.e., about 11,000K in a nitrogen arc at atmospheric pressure [20, 21].

• Others [23] have used Rayleigh scattering to determine the deviation of the gas temperature from the electron temperature in arc boundaries, where the degree of ionization is lower.

A thorough study and comparison of most of these methods is not available.

Research Needs

In general, models are available to determine the status of plasmas using non-LTE diagnostic methods. Research which assumes LTE without proper proof should be discouraged. Research to validate non-LTE diagnostic methods should be encouraged for determination of T_g, T_e, N_a, and the appropriate form of the ionization equation for various plasma regimes. Technical workshops for the presentation and discussion of non-LTE diagnostic methods would reduce the time for more common use.

References

1. L. Bober and R.S. Tankin, J. Quant. Spectrosc. Radiat. Transfer, 9, 855-874 (1969) and 10, 991-1000 (1970).

2. M.P. Freeman and S. Katz, J. Opt. Soc. Am., 50 (8), (1960).

3. A. Sedghinasab, T. L. Eddy, R. T. Murray and A. V. Larson, Rev. Sci. Instr., 57 (8), 2093-95 (1986).

4. H. R. Griem, Plasma Spectroscopy, McGraw Hill, N.Y., (1964). a) pp 176-8 b) pp 268-9 and 293-5.

5. S. I. Herlitz, Ark. Fys., 23 571 (1963).

6. C. D. Maldanado and H. N. Olsen, J. Opt. Soc. Am., 56, 1305 (1966).

7. D. N. Ghosh Roy, J. Quant. Spectrosc. Radiat. Transfer, 31, 15 (1984).

8. P. Baessler and M. Kock, J. Phys. B, 13, 1351 (1980).

9. T. L. Eddy, E. Pfender, and E.R.G. Eckert, IEEE Trans. Plasma Sci., 1, 31 (1973).

10. T. L. Eddy, J. Quant. Spectrosc. Radiat. Transfer, 33(3), 197-211 (1985).

11. H.R. Griem, A.C. Kolb and K.Y. Shen, Astrophys. J., 135, 272 (1962).

12. C. R. Vidal, J. Cooper, and E. W. Smith, Astrophys. J. Suppl. No. 214, 25, 37 (1973).

13. K. Y. Cho and T. L. Eddy, Paper EA-4, 39th Gaseous Electronics Conf., Madison, Wisc., Oct. (1986).

14. T. L. Eddy, A. Sedghinasab, K.Y. Cho, and R. V. Frierson, "Radiative Properties of Non-LTE Plasmas," Final Report, NSF Grant CPE-8311325, in preparation (1987).

15. M. Boulos, P. Fauchais and E. Pfender, Diagnostic Techniques in Thermal Plasma Processing, Part II, pp. 267-281, DOE/ER-0270, NTIS, U.S. Dept. Commerce, Springfield, VA (1986).

16. T. L. Eddy, C. J. Cremers, H. S. Hsia, J. Quant. Spectrosc. Radiat. Transfer, 17, 287-296 (1977).

17. H. Kafrouni, Physica 98C, 100-112 (1979).

18. A. Gleizes, H. Kafronni, H. Dang Duc and C. Maury, J. Phys. D: Appl. Phys., 15, 1031-1045 (1982).

19. K. P. Nick, J. Richter and V. Helbig, J. Quant. Spectrosc. Radiat. Transfer 32(1), 1-8 (1984).

20. J. M. Baronnet, "Etude comparative de méthodes de mesure de la temperature de rotation vibration de la molecule N_2^+ dans un plasma d'azote produit par un générateur à arc," Thèse de 3ème Cycle, Univ. of Limoges, France (1971).

21. J. F. Coudert and P. Fauchais, Paper P-9-5, Proc 7th Int'l. Symp. Plasma Chem., v. 3, pp. 760-763 (1985).

22. G. Traving, "Interpretation of line broadening and line shift," Ch. 2, Plasma Diagnostics, (Ed.) W. Lochte-Holtgreven, North Holland Publ. Co., Amsterdam (1968).

23. G. H. Haddad, A.J.D. Farmer, L.E. Cram, and J.J. Lowke, "Departures from LTE of Free-Burning Arcs in Argon," Paper EA-1, 39th Gaseous Electronics Conf., Madison, Wisc. Oct. 1986.

24. T. L. Eddy, A. Sedghinasab and P. L. Johnson, Proc. 7th Int'l. Symp. Plasma Chemistry, v. 3, pp. 772-777, (1985).

25. M. Boulos, P. Fauchais and E. Pfender, Diagnostic Techniques in Thermal Plasma Processing, Part I, pp. 169-171, DOE/ER-0270, NTIS, U.S. Dept. Commerce, Springfield, VA. (1986).

26. D. Schlüter, Z. Phys., 210, 80 (1968).

27. D. Hofsaess, J. Quant. Spectrosc. Radiat. Transfer, 19, 339 (1978).

7.3 PARTICLE DIAGNOSTIC TECHNIQUES

MAHER I. BOULOS
Department of Chemical Engineering
University of Sherbrooke
Sherbrooke, Quebec, J1K 2R1

Introduction

The in-flight heating and melting of particles under plasma conditions whether for powder spheroidization, spray coating or chemical synthesis depends strongly on the proper control of the particle trajectory and their temperature history during their short residence time in the plasma stream. Our understanding of the basic phenomena involved depends largely on the availability of appropriate diagnostic tools for the measurement of the plasma and the in-flight, particle parameters, and the development of comprehensive theoretical models of the processes involved. In this note, a brief discussion is presented about available particle diagnostic techniques and research needs in this area. A general review about gas and particle diagnostics under plasma conditions is given in [1].

Particle Parameters

These can be grouped as follows, depending on whether the measurement is carried out on a collected sample of the powder or in-flight.

For a collected sample, the principal parameters which can be measured are: Particle diameter, shape, specific surface, porosity, microstructure, chemical composition, etc. These can be carried out by optical and electron microscopy associated with image analysis, X-ray diffraction, light scattering, atomic absorption, ICP spectrochemical analysis and neutron activation techniques. A detailed discussion of these techniques is beyond the scope of this note.

In-flight measurements of the particle parameters are generally more difficult. The principal parameters needed are: Particle velocity, surface temperature, diameter and number flux distributions. A distinction should be made between obtaining statistical information about each of these parameters at a time and the simultaneous measurement of these parameters for each particle crossing the observation volume. In the latter case, the information obtained can be used for the determination of cross-correlations between the different parameters.

Available, In-flight Particle Diagnostic Techniques

Particle velocity

Cine and streak photographic techniques have been gradually replaced by powerful, microprocessor-controlled, laser Doppler anemometry. These have been used successfully under plasma conditions for the determination of one and two-velocity components. Its principal limitation is still related to its sensitivity to background radiation. Velocity measurements in the high temperature core of the arc or a d.c. plasma jet has been difficult to achieve. Proper seeding, for plasma velocity measurements, is also a problem.

Particle surface temperature

Only recently, encouraging results on in-flight, particle surface temperature measurements have been reported using two-color pyrometry. The principal

limitations of the technique are; sensitivity to background plasma radiation and electrical noise, and the limited range of particle temperatures that could be measured. The technique is applicable only under dilute particle-loading conditions to avoid having more than one particle in the measurement volume at the same time.

Particle diameter

This has mostly been carried out based on the Mie scattering theory. Few techniques have been tested for the in situ particle diameter measurement under plasma conditions. The main difficulties are due to the dependence of the intensity of the scattered light on that of the incident laser beam and the optical properties of the particles. The theory has only been developed for spherical particles. Other limitations are similar to that of particle surface temperature measurements including the sensitivity to the background plasma radiation and the applicability of the technique to dilute particle loading conditions.

Particle number flux

This is usually combined with any of the other particle parameter measurement techniques and shares their limitations. Measurements are carried out by simply counting the particle pulse rate. Particle flux distributions can also be determined through the collection of the material on a target for a short exposure time. This technique, however, will only apply to situations when the particles are completely molten.

Areas Where a Specific Research Effort is Needed

- Incorporation of fiber optic technology into the measurement technique in order to transmit the signal from the plasma to the detector, thus reducing electronic noise problems.

- Development of appropriate techniques for the simultaneous measurement of more than one particle parameter.

- Developments of new measurement techniques for dense particle cloud diagnostics under plasma conditions.

References

1. M. I. Boulos, P. Fauchais and E. Pfender, "Diagnostic techniques in thermal plasma processing", DOE report ER-0270, February (1986).

7.4 LASER DIAGNOSTIC TECHNIQUES

M. E. McILWAIN
Idaho National Engineering Lab
EG&G Idaho, Inc.
Idaho Falls, Idaho 83415

Laser-based diagnostic methods are particularly suited for nonintrusive characterization of thermal plasma processing environments. These plasma environments are typically characterized as being turbulent, luminous, and highly particulate laden. These characteristics pose serious detection problems to most steady state optical measurements. The incorporation of a laser light source into a typical optical method affords enhanced spectral sensitivity, since the resulting emission signals are greatly increased in intensity or the signal has an inherent temporal property which can be used to discriminate the desired light signal relative to the plasma background [1].

Flow Characterization

Various photographic based techniques have been widely used to obtain both qualitative and/or quantitative data concerning the fluid dynamics associated with high-temperature, flowing environments. Relatively simple methods, such as shadow and Schlieren photography have been employed to ascertain flow patterns, gas density and turbulence in both combustion and plasma heated gases [2,3]. Interferometric based methods have also found wide application for characterization of both fluid and particulate dynamics [4]. The incorporation of holographic image recording methods with classical interferometry can greatly increase the sensitivity and spatial resolution while reducing the degree of background interferences [5].

The advantages of shadow and Schlieren photography are that the cost of the equipment is low, the optical configuration is easy to construct, and the level of operator expertise is minimal. Holographic and classical interferometry pose slightly more complex optical configurations, but again, require a relatively low degree of operator expertise.

The disadvantage of this type of measurement is that it is a line-of-sight determination. This is always true for shadow and Schlieren methods. This preferred two-dimensional geometry results in complex images representing a sum of all contributions across the line-of-sight. Only relatively simple cases can be treated mathematically to deconvolute the images into three-dimensional data. Holographic interferometry offers the potential for greater spatial resolution, however, the complexity of the optical configuration is such that one typically does not attempt highly spatially resolved measurement. Therefore, one is again faced with images representing relatively large volumes.

Species Composition

Determination of species composition, as well as density, can be performed using simple Raman scattering, coherent anti-Stokes Raman scattering (CARS) and laser-induced fluorescence.

In general, Raman scattering is extremely useful for determination of molecular and certain atomic species which do not absorb in the regions of the spectrum accessible using laser light sources. The Raman technique has the

advantage of being highly species specific, has a well established theory, and has extremely high spatial resolution. In this case, the spatial resolution is defined by the beam waist of the excitation laser and the width of the slits of the detection monochromator. In the case of CARS, the spatial resolution is defined by the volume of overlap between the two pump and Stokes excitation beams [6].

The principle disadvantage of Raman methods is the relatively high cost, significant level of operator expertise, and significant background contribution associated with free electrons in the plasma. In addition, high levels of particulate loading can obscure both the light passing into and out of the plasma.

Laser-induced fluorescence has the advantage of high species selectively, high spatial resolution, temporal resolution, and in certain cases, can yield quantitative information. Using planar laser-induced fluorescence methods, three-dimensional species compositions and flow properties can be accurately obtained [7].

The main disadvantages of laser-induced fluorescence are the extremely high cost of the method, the high degree of operator expertise, and the need to have materials which absorb light in the visible or near ultra-violet regions of the spectrum.

Particulate Composition

The composition of particulate material in flight can be determined using laser-induced breakdown (or laser-spark breakdown). A typical system requires a laser source with sufficient intensity to breakdown air or create a spark on the surface of a particle. When the spark is created on the surface of a particle, material is evaporated off of the surface and heated to extremely high temperatures. The resulting light emission from this high temperature medium will be representative of the atomic composition of the particle and the plasma gas [8].

The advantage of laser-breakdown spectroscopy is real-time species identification, simplicity of operation, and low cost. The main disadvantage is that certain elements can not be determined using this method, and particulate loading must be sufficient to cause a sufficiently large number of breakdowns to occur so that sufficient emission intensity can be collected to characterize all elements present in the particle.

Research Needs

For laser-based diagnostics, as well as conventional emission diagnostics of thermal plasmas, additional information is needed on:

- High-pressure atomic transition probabilities.
- Electron excited-state collision cross sections.
- High-pressure collision-broadening theory.
- Quantum efficiencies.

References

1. D. R. Crosley (ed.), Laser Probes for Combustion Chemistry, ACS Symposium Series 134, American Chemical Society, Washington, D.C., (1980).

2. F. J. Weinberg, Optics of Flames, Butterworths, London, (1963).

3. A. G. Gaydon, Spectroscopy and Combustion Theory, Chapman & Hall, London, (1948).

4. J. D. Trolinger, Laser Instrumentation for Flow Field Diagnostics, AGARD-AG-186, (1974).

5. M. E. McIlwain, J. F. Key, and L. D. Reynolds, Holographic Interferometric Analysis of Electrically Driven Plasmas, High Temperature Science, 20, 21, (1985).

6. A. C. Eckbreth and P. W. Schreiber, Coherent Anti-Stokes Raman Spectroscopy: Applications to Combustion and Gas-Phase Diagnostics, Chemical Applications of Nonlinear Raman Spectroscopy, A. B. Harvey, ed., Academic Press, New York, (1981).

7. M. E. McIlwain and S. C. Snyder, unpublished results.

8. M. Boben and J. Singer, High Temperature Vapor Pressure of Metals from Laser Evaporation, High Temperature Science, 19, 329, (1985).

THERMAL PLASMA RESEARCH AREAS

CHAPTER 8

THERMOPHYSICAL PROPERTIES

Session Chairman

Alan V. Larson
Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

8.1 THERMOPHYSICAL PROPERTY OVERVIEW

ALAN V. LARSON
Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Introduction

In the ideal world, a computer would input the device configuration, the mass inputs, the power inputs and would predict correctly the mass and power outputs and the spatial and temporal details of the process. The computer would have three files: DEFINITIONS, PRINCIPLES, DATA BASE. The latter would hold the characteristics of matter and radiation which are called Properties for our purpose.

Hypothesis
The Principles for Plasma Processing are known but the Data Base is inadequate.

Discussion
There is general agreement that the data base is inadequate. There are questions on whether the principles are known for handling:

Strong departures from equilibrium
Turbulence
Fluctuations
Radiation Transport
Effects of Electromagnetic Fields,

especially in particle-laden flows.

For example, consider a solid pellet in an inhomogeneous plasma. The intermediate zone is ill-defined because the pellet tends to charge negatively and the surface may undergo chemical/physical changes with concurrent concentration changes in the zone. How then can we choose the thermal conductivity, the diffusion coefficients, the surface emissivity, or the reaction rates?

Thermal plasma processing in the gas phase avoids that problem. Chemical and physical nonequilibrium remain. How do we choose the enthalpy, entropy and the transport coefficients, for example? Multitemperature models may suffice if each energy mode is independent and has a well characterized energy distribution. Spectroscopic interpretations may be based on the distribution model - so they are coupled into the problem and therefore are not independent.

The other listed problems may also be significant in gaseous plasma processing.

Research Needs

At present, specific needs are very much dependent on the particular application and its devices. To find general understanding, systematic studies should be encouraged on each type by a multidisciplinary team with sufficient breadth of knowledge. An adequate mix might consist of the following fields:

Plasma chemistry
Fluid dynamics
Metallurgy
Spectroscopy
Finite element analysis
Apparatus engineering
Technician.

The goal is to arrive at a detailed description of the process sufficient to contribute to generalized design knowledge.

The need for property data by such teams should be published so that individual workers or smaller teams could devise means to find the appropriate property values.

The plan is not new. It has been followed in the related fields of atmospheric entry, combustion and fusion.

State of the Art

Mostly Equilibrium or Quasi-Equilibrium

Table I classifies some properties and recent references. Each class tends to depend on one or more above it in the table. The references are illustrative, but few in number. Critically evaluated tabulations of data on a given property may exist in a data journal such as Ref. [1]. The references internal to Ref. [1] may be studied for experimental or calculational techniques. Only recent trends or events need be outlined.

Calculations continue using molecular data to obtain partition functions and then equilibrium thermodynamic properties. The molecular interaction potentials lead to evaluation of collision integrals which are used in advanced kinetic theory to calculate the transport properties. Thermochemical kinetics [7] can lead from molecular potential energy surfaces to thermodynamic data, and given the heats of formation provides an estimation of products and reaction rates.

The self-consistent field method has been applied [13], to the coupled vibrations of polyatomic systems with application to the spectroscopy of highly excited states and is expected to be useful in molecular dynamics, energy flow, and mode specificity in chemical reactions. Rovibrational levels have been predicted accurately with ab initio potentials in a Morse-oscillation model for D_2 and H_2 [2], and the technique may be useful for all hydrides. A sophisticated approximation to the partition function of free internal rotation has been examined for nonnegligible error in the calculation of enthalpy, entropy, and specific heats [4]. A new model for intermolecular potentials is discussed in Ref. [3] which bypasses some problems of existing models.

References [5, 14, 25, 38] are examples of calculations of equilibrium thermodynamic properties and transport properties of pure gases using conventional advanced methods. Examples for mixtures are found in Ref. [6, 15-21, 39].

Table I Thermophysical Property Sources: Recent References (Non-inclusive)

ISOLATED MOLECULE	
Energy Levels, Statistical Weights	1, 13
Energy Modes	
Potential Energy Surface	13
Radiation Probabilities	1
MOLECULE + X	
Interaction Potentials	2, 3, 10
Scattering cross section	
Collision Integrals	
Activation Energy	
Reactions, Rates	41
Work Functions (S)	
Reflection/Sticking (S)	
PARTITION FUNCTIONS	
Single Particles	4
Ensembles	
PURE GAS: EQUILIBRIUM THERMODYNAMICS	
P, T, ρ, N_i	1, 5, 6
Equation of State	
Internal Energy (R,V,E)	
Enthalpy "	
Entropy "	
Specific Heats "	
PURE GAS: TRANSPORT PROPERTIES	5, 14, 25, 38
Viscosity	1
Thermal Conductivity	1
Electrical Conductivity	
MIXTURES	15 - 21
Equilibrium Thermodynamic Properties	1
Transport Properties, Including Diffusion	1, 39
Reactions	
THERMOCHEMICAL KINETICS	7 - 12
Concentrations	
Heat of Formation	
Entropies	
Elementary Reaction Steps	1
Reaction Rates	1
NON-EQUILIBRIUM SYSTEMS	22, 23
Two Temperature	24, 25
Multi-Temperature	26, 27
Kinetic modeling	28 - 30
Particle Laden	31, 32, 41
RELATED LITERATURE	
Atmospheric Entry	33, 35, 36, 39
Combustion with Spray or Soot	34, 37
Fusion with Pellets	

Evidence now shows that certain reactant states (T, V, R, E) lead to specific ensembles of product states, Even geometric orientation and alignment of the species relative to each other can cause differences in reaction cross section and product expectations. These finds have stimulated work on the selectivity of elementary processes. Examples are given for H + CO_2 and CN + H_2 and others [8,9].

The data on molecular ion vibrational excitation and relaxation is sparse. Ion drift tubes have been built for systematic studies [10]. New insights have been gained into ion-molecule interaction potentials.

A promising research philosophy [12] examines, experimentally, the same elementary chemical process over a wide range of densities from the low pressure gas into the compressed liquid phase. Rate coefficients, transient state populations, and quantum yields are measured. The gas pressure provides an "internal clock" for "collisional times". Another pressure dependence is examined in Ref. [11] for the influence of vibrational relaxation on unimolecular rate constants.

Mostly Nonequilibrium

Reference [22] reviews models developed to explain the importance of vibrational nonequilibrium in plasma chemistry reactions. The formalism of extended irreversible thermodynamics is used to develop equations to study how the heat and diffusive fluxes influence the development of a chemical reaction under given boundary conditions [23].

Two temperature modeling [24, 25] and multitemperature analysis [26, 27] have been applied to plasma systems. Each subsystem is characterized by an energy distribution parameter, T, and then each subsystem is treated as if in equilibrium.

Kinetic modeling [28, 29, 30] attempts have related the velocity, temperature, and species composition along a stream line via a reduced set of chemical reactions and their reaction rates. T is the gas temperature. Diffusion was neglected in Refs. [24-30].

The study of particle laden nonequilibrium systems in plasma processing has just begun [31, 32, 41].

Related Fields

Atmospheric entry [33, 35, 36, 38, 39, 40] is a well developed field with an extensive history. In many ways it is similar to plasma processing, even in the types of molecules. The computer codes are extensive, say 28 species, and expensive to run. Lately, attempts [35, 39] have been made to find approximations to thermodynamic and transport subroutines which are accurate enough for parametric studies and design studies yet less demanding of computer time and storage.

Combustion with spray or soot [34, 37] is an important allied field which was not reviewed for this workshop. Neither was the field of fusion with pellets reviewed.

References

1. "Cumulative Listing of Reprints and Supplements," Journal of Physical and Chemical Reference Data, 15, 933 (1986).

2. Huffaker, J. N. and Cohen, D. I., "Accurate Analytic Model Potentials for D_2 and H_2 Based on the Perturbed Morse Oscillator Model," J. Chem. Phys., 85, 346 (1986).

3. Roeggen, I., "Intermolecular Potentials Calculated by an Extended Geminal Model: Theory," J. Chem. Phys. 85, 1 (1986).

4. Slamina, Z., "Once Again on the Partition Function of Free Internal Rotation: Rigorous Results," J. Phys. Chem., 90, 2957 (1986).

5. Hsu, K. C. and Pfender, E., "Modeling of a Free-Burning High Intensity Arc at Elevated Pressures," Plasma Chem. and Pl. Proc., 4, 219 (1984).

6. Degout, D., et. al., "Titanium Dioxide Plasma Treatment," Plasma Chem. and Plasma Proc., 4, 179, (1984).

7. Walsh, R., "Thermochemical Kinetics: A Success Story," J. Phys. Chem., 90, 389 (1986).

8. Buelow, S., et. al., "The Role of Initial Conditions in Elementary Gas-Phase Processes Involving Intermediate 'complexes'", J. Phys. Chem., 90, 1015 (1986).

9. Rice, S., "Selectivity of Elementary Molecular Processes Associated with Energy Transfer and Chemical Reaction", J. Phys. Chem., 90, 3063 (1986).

10. Ferguson, E., "Vibrational Quenching of Small Molecular Ions in Neutral Collisions", J. Phys. Chem., 90, 731 (1986).

11. Borkovec, M., et. al., "The Influence of Intramolecular Vibrational Relaxation on the Pressure Dependence of Unimolecular Rate Constants," J. Chem. Phys., 85, 146 (1986).

12. Troe, J., "Elementary Reactions in Compressed Gases and Liquids: From Collisional Energy Transfer to Diffusion Control," J. Phys. Chem., 90, 357, (1986).

13. Ratner, M. A. and Gerber, R. B., "Excited Vibrational States of Polyatomic Molecules: The Semiclassical Self-Consistent Field Approach," J. Phys. Chem., 90, 20 (1986).

14. Mazor, et. al., "A Simple and Accurate Expression for the Viscosity of Nonpolar Diatomic Gases up to 10,000K", AIAA J., 23, 636 (1985).

15. Bacri, J., et. al., "Equilibrium Composition and Thermodynamical Potentials of Nitrogen-Oxygen Mixtures," Proc. 7th Int. Symp. on Plasma Chem., 880 (1985) Eindhoven.

16. Baronnet, et. al., "Transport Coefficients of High Temperature H_2, O_2 Plasma, Ibid., p. 836.

17. Gleizes, et. al., "Calculation of Thermodynamic Properties and Transport Coefficients for SF_6 - N_2 Mixtures in the Temperature Range 1,000-30,000K". Plasma Chem. and Pl. Proc., 6, 65 (1986).

18. Gleizes, et. al., "Transport Coefficients in Arc Plasma of SF_6-N_2 Mixtures," J. Appl. Phys., 54, 3777 (1983).

19. Wilhelmi, et. al., "Calculation of Thermodynamic and Transport Properties of a Typical Arc Furnace Plasma," Plasma Chem. and Pl. Proc., 4, 315 (1984).

20. Plotezyk, W., "Thermodynamic Models of Acetylene Synthesis in an Argon Plasma Jet," 7th Int. Symp. on Plasma Chem., Proceedings, 280 (1985), Eindhoven.

21. Weigel, A., "Experiments on the Reduction of Iron Ores with an Argon-Hydrogen Plasma," Ibid. 1214.

22. Capitelli, M., "Progress in the Kinetics of Chemical Reactions in Non-Equilibrium Plasmas," Pure and Appl. Chem., 52, 1721 (1980).

23. Garcia-Colin, L. S., et. al., "Consistency of the Kinetic Mass Action Law with Thermodynamics," J. Phys. Chem., 90, 953 (1986).

24. Mostaghimi, J., et. al., "A two-temperature Model of the R. F. Inductively Coupled Plasma," 7th Int. Symp. Plasma Chem., Proceedings, 865 (1985), Eindhoven.

25. Chen, D. M., et. al., "Two-temperature Modeling of an Arc Plasma Reactor," Plasma Chem. and Pl. Proc., 3, 295 (1981).

26. Eddy, T. L., "Effect of Cold Gas Injection on Plasma Temperature Measurements," 7th Int. Symp. on Plasma Chem., Proceedings, 772 (1985), Eindhoven.

27. Eddy, T. L., and Pruitt, D. W., "A Multithermal Equilibrium (MTE) Arc Plasma Heat Transfer Model," 37th Gaseous Electronics Conf. Proc. (1984), Boulder.

28. Skrebov, et. al., "Kinetics of Excited Atoms in Non-Stationary Non-Equilibrium Plasma of Inert Gases with Account of Ionic-Molecular Reactions," 7th Int. Symp. on Plasma Chem. Proceedings, 1416 (1985), Eindhoven.

29. Spangenberg, H. J., "Physico-Chemical Conditions During the Pyrolysis of Hydrocarbons in a Plasma Jet," Ibid., 291.

30. Coudert, J. F., "Kinetic modeling of the Reduction of $SiCl_4$ in a Arc Heater for the Production of Silicon," Plasma Chem. and Pl. Proc., 2, 399 (1982).

31. Zhukov, M. F., et. al., "Joint Physical and Computational Experiment and Research Problems of High Temperature Dust Laden Jets," 7th Int. Symp. on Plasma Chem. Proceedings, 856 (1985), Eindhoven.

32. Pfender, E., "Heat and Mass Transfer to Particles in Thermal Plasma Flows," Ibid, 20.

33. Yucel, A., et. al., "Radiative Heat Transfer in Absorbing, Emitting, and Anisotropically Scattering Boundary Layer Flows, AIAAJ, 22, 1162 (1984).

34. Nelson, H. F., "Influence of Particulates on Infrared Emission from Tactical Rocket Exhausts," J. of Spacecrafts and Rockets, 21, 425 (1984).

35. Zoby, E. V. and Moss, J.N., "Thermodynamic Equilibrium-Air Correlations for Flowfield Applications," AIAAJ, 20, 849 (1982).

36. Swaminathan, S., et. al., "Effects of Slip and Chemical Reaction Models on Three-Dimensional Nonequilibrium Viscous Shock-Layer Flows," J. Spacecraft, 521 (1984).

37. Look, Jr., D. C., "Effective Radiation Scattering Coefficient," AIAAJ, 19, 666 (1981).

38. Rainwater, J. C., et. al., "Numerical Calculation of Gaseous Transport Properties from the Hulbert-Hirschfelder Potential with Applications to Planetary Entry Thermal Protection," Progress in Astro. and Aero., 82, 3 (1982). (Monatomic Carbon).

39. Armaly, B. F. and Sutton, K., "Thermal Conductivity of Partially Ionized Gas Mixtures," Ibid, 53.

40. Goulard, R., "Nondimensional Parameters in Radiation Gas Dynamics," Ibid, 83.

41. Meubus, P., "Effects of UV Light Irradiation on Propane in an Argon Plasma," Plasma Chem. Plasma Proc., 6, 143 (1986).

8.2 CALCULATING LTE THERMODYNAMIC AND TRANSPORT PROPERTIES OF HIGH TEMPERATURE PLASMAS

RICHARD W. LIEBERMANN
GTE-Sylvania Lighting Center
Danvers, Massachusetts 01923

Introduction

Analytical modeling of high temperature plasmas requires solving time dependent sets of nonlinear differential equations that describe the conservation laws of mass, momentum, and energy, satisfy the laws of diffusion, define the equation of state, and satisfy imposed boundary conditions [1]. In general, these expressions involve knowing material properties of the medium. Such parameters include the plasma's thermal and electrical conductivity, viscosity, spectral absorptivity, heat content (enthalpy), specific heats, density, and chemical reaction rates. As can be visualized, solving these models may prove to be a formidable task. However, the situation is somewhat alleviated by assuming conditions of local thermodynamic equilibrium (LTE). This approach will not always be valid, but it may provide a valuable insight of trends.

In the following presentation, we will examine the present methods for calculating material properties of high temperature plasmas in LTE. In particular the presentation will be divided into two parts. The first part will examine thermodynamic properties, while the second part will examine the transport properties.

Thermodynamic Properties

The heat content, density, and specific heat (and transport properties) of an isothermal gas mixture (in LTE) are functions of the gas temperature, pressure, and the chemical species concentrations. The latter are determined by utilizing the chemical equilibrium relationships.

Chemical Equilibrium Calculations

In computations of the fifties, the species' concentrations were determined by solving a set of nonlinear equations that satisfy the laws of mass action, total pressure, charge neutrality, and local conservation of mass [2,3]. In this time frame most calculations were performed on hand calculators, whence, the number of chemical species considered in a given the gas mixture were limited. Input to these calculations included equilibrium constants for each specified chemical reaction or instead partition functions of each chemical species therein, plus the reactant species' dissociation or ionization energies. In the latter case, the partition functions were (in many cases) calculated through an iterative scheme to establish a self consistent, pressure dependent "cut off" of the electronic contribution.

In the early sixties, a more powerful method for solving chemical equilibrium problems emerged [4,5,6,7]. This method was geared to compute the concentrations of chemical species (in a seemingly unlimited, multicomponent, gas mixture) by minimizing the mixture's Gibbs free energy while satisfying charge neutrality and the imposed mass constraints. In this method, the only physical properties required for input are the chemical species standard Gibbs free energy [7]. And of particular advantage over earlier methods: the minimization method does not require formal declaration of the chemical reactions taking place.

It was not until the late sixties that minimization codes became adjusted to handle multicomponent, polyphase chemical mixtures [8]. Since then, several other codes have been so modified [9,10,11,12]. It is realized that computer program development is expensive, and that most potential users look "outside" to see what is available. One of the more popular programs in use is the NASA Lewis Program [9]. This free energy minimization program is available (for a slight handling fee) on tape, including a data bank (of chemical species free energy data) and instructions. Other data banks (commercial) are also available but for a contract fee. See references 33 and 34, for example.

A good review of past and present "in house" chemical equilibrium programs, is given in reference [12]. While a good review of chemical equilibrium programs that consider effects due to diffusive and convective flows is made in reference [14]. This latter review focuses in on the arc vapor lamp technology. Reference [13] also gives a review on "in house" chemical equilibrium programs, but in addition lays out a means for eliminating redundant computer programming and/or redundant data bank development.

Gibbs Free Energy

As pointed out above, calculations of chemical species' concentrations require knowing thermodynamic properties of each individual species in the mixture. For the minimization process, input of the species' standard molar Gibbs free energy is required. For a given chemical species, the molar Gibbs free energy is:

$$G = H - T*S \tag{1}$$

where H is the heat content, T is the gas temperature and S is the entropy. The molar heat content is expressed as:

$$H(T) = \int_{298}^{T} C_p dT + \Delta H_f(298) \tag{2}$$

where the first term represents the species' sensible heat or enthalpy as a function of the specific heat, C_p, and the second term $\Delta H_f(298)$ represents the species' standard enthalpy of formation in term of its elements in their standard state at 298.15 K. The species' molar entropy is expressed as:

$$S(T) = \int_{298}^{T} (C_p/T)dt + S(298) \tag{3}$$

As noted, the standard Gibbs free energy can be determined for a given chemical species when values of $C_p(T)$, $S(298)$ and $\Delta H_f(298)$ are known. It is fortunate that many chemical species of general interest have values reported in the literature [15-32]. However, most values are tentative and subject to changes, i.e. when more reliable data presents itself. For creators of Data Banks, this requires adoption of continuous but suitable update procedures. Computer-assist evaluation of thermochemical data is described in references [35 and 36]. In general, many species' data are reported in the form of $C_p(T)$, $H(T)$, and $S(T)$. But for convenience of handling vast amounts of data in compact form, the species' thermodynamic properties are usually represented in terms of a Cp(T) function. That is, the C_p values are analytically curve fitted to a temperature model from which values of $H(T)$, $S(T)$, and $G(T)$ are easily obtained. A general form of this model is [5,6,8,16,20,21]:

$$Cp(T) = a + b*T + c*T^2 + d*T^3 + e*T^{-2} \quad (4)$$

and requires use of a computerized multi-regression (least square) routine. From my own experience, some chemical species may require several curve fits that represent adjacent temperature ranges to insure minimum deviation of say, less than one tenth of one percent. Such an approach is employed by reference [8].

Other literature data provides molecular constants (vibrational frequencies, rotation constants, etc.) for gaseous molecules [15,23,24,27,28]. Using ideal gas models [1,15], standard functions of $C_p(T)$, $H(T)$, and $S(T)$ can be generated, tabulated, and/or analytically curve fitted. In many instances, users of minimization programs, do not find complete sets of thermodynamic properties (in the literature) for their prime chemical species of particular interest. This leads to estimates. The latter approach becomes the rule rather than the exception when state of the art investigations are underway. In any case, "ready or not", the user finds himself in the position of trying to be an expert, i.e. deciding which information best represents the true values. An evaluation program of the type described in reference [36] would then prove useful.

Mixture Properties

Once the chemical species concentrations are determined, thermodynamic properties of the gas phase are calculated by standard means. In quick review, those properties of immediate interest are defined as:

$$[H(T)]mix = \sum_i X_i H_i(T) \quad (5)$$

$$[C_p(T)]mix = \left.\frac{\partial [H(T)]mix}{\partial T}\right|_p \quad (6)$$

$$\rho = \sum_i \rho_i \quad (7)$$

where X_i are molar fractions and ρ_i are mass densities of each gas species. The species' heat content, $H(T)_i$, is defined in equation (2).

General Comments

The above review shows the trends of calculating chemical equilibria over the past few decades. Minimizing the Gibbs free energy is a constant pressure process. However, a slight modification of computer code (an iterative routine on pressure) allows the Helmholtz free energy to be minimized. The latter approach simulates conditions of constant gas density or volume. In either case, the only input required is the standard Gibbs free energy functions of each participating chemical species. In similar fashion, added iterative schemes allow for lowering of ionization potentials and inclusion of viral corrections to the equation of state, plus the modeling of activity coefficients for solid or liquid substances in solution. The only fallacy is in considering the chemical species thermodynamic properties as independent of pressure, that is, by generating $C_p(T)$

functions using fixed arbitrary "cut offs" for the gas species' internal partition functions. The chemical species' thermodynamic properties are strong functions of the internal partition functions. Hence, an iterative "cut off" correction should be incorporated in the minimization programs. This, of course, will require electronic energy levels of the chemical species to become part of the user's data bank format.

Transport Properties

Thermal and Electrical Conductivity, and Viscosity Formulae

Transport properties of multicomponent gas mixtures in LTE are calculated using the rigorous kinetic theory of gases [1,37]. Chapman-Enskog approximations [1,38-41] are used to calculate the viscosity, and the thermal and electrical conductivity. The electrical conductivity is also calculated by solving the electron mobility integral [42-45]. In the mobility integral, the electron velocity distribution is assumed Maxwellian. However, modifications are made through use of a Spitzer-Harm gamma function [46] to force agreement, at elevated temperatures, between these conductivity results and those of a fully ionized gas. The reactive contribution to the thermal conductivity is calculated using the Brokaw formulae [38]. For nonconvective gases, this contribution becomes independent of model geometry. When convective flow is important, the reactive term should be calculated as the local diffusive fluxes are established.

The above transport formulae are functions of each gas species' concentration value, their masses, and their gas kinetic cross sections. Algorithms for calculating transport coefficient of gas mixtures in LTE, should allow the user to specify an intermolecular potential for each gas species - gas species interaction of which force constant (or impact parameters) have been experimentally measured [1]. This provides fast calculations of "effective" cross sections (averaged over velocity). For example, many neutral-neutral interactions can be described in terms of a Lennard Jones 6-12 potential [1], others by an exponential six potential [47], or a regular exponential potential [48], also a Stockmayer potential [49], or a Morse Potential [50]. A repulsive or attractive screen Coulomb potential [51] is used for the charge-charge interactions. Other interactions involving the inverse power potential [52,53], and the charge transfer potential [40,54] are included. Momentum transfer cross sections (as a function of electron energy) are required for solving the mobility integral.

Cross Section Data

Values of collision cross sections are reported in the literature for a wide variety of interactions. A tentative list of investigators reporting values is given [55-74]. However, it is pointed out that many discrepancies are present. Efforts have been underway at JILA to sort out reliable data [56].

General Comments

A generalized LTE Transport program has been developed by this author with most all features described above, including a data bank of cross sections and impact parameters. The transport results have been compared to experimental measurements when possible. The impact parameter approach gives good results for low temperature ($<$2500K) data. Electrical conductivity values of pure gas mixtures also show good agreement with available data. At low gas temperatures the mobility integral appears to give values of electrical conductivity that are in better agreement with measurements than those values determined using the first Chapman-Enskog approximation. Several comparisons have been made with properties of the more complex mixtures, i.e. SF_6. The comparisons were less favorable at

the higher temperatures (within say a factor of two or three for T > 8000 K). However, diffusion and convective effects were not taken into account. A more controlled set of experimental data would be helpful.

References

1. J. O. Hirschfelder, C. F. Curtiss, and R. F. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons Inc., New York, 1964.

Chemical Equilibrium Programs

2. J. Hilsenrath, M. Klein, and H. W. Wooley, "Tables of Thermodynamic Properties of Air Including Dissociation and Ionization from 1500 K to 15000 K", Arnold Engineering Development Center, AEDC-TR-59-20, MIPR-AEDC-2, OSS 59-24, National Bureau Standards, 1959.

3. J. Hilsenrath and Max Klein, "Tables of Thermodynamic Properties of Air in Chemical Equilibrium Including Second Viral Corrections from 1500 K to 15000 K", Arnold Engineering Development Center Air Force System Command, AEDC-TR-G5-58, ADG12301, 1965.

4. W. P. White, S. M. Johnson, and G. B. Datzig, Chemical Equilibrium in Complex Molecules, J. Chem. Phys., 28, 751, 1958.

5. J. Warga, "A Convergent Procedure for solving the Thermo-Chemical Equilibrium Problem", AFBSD,AD #286766, 1962.

6. R. G. Stern, "A Thermochemical Equilibrium Machine Program", AFBSD, AD #288664, 1962.

7. A. R. Hochstin, "Theoretical Calculations of Thermodynamic Properties of Air", 5th AGARD Combustion and Propulsion Colloquium, Pergamon Press, pp. 3-44, 1963.

8. J. J. Lowke, M. A. Uman, and R. W. Liebermann, "Toward a Theory of Ball Lightning", J. Geophysical Research, Vol. 74, G887-98, 1969.

9. S. Gordon, Complex Chemical Equilibrium Calculations, NASA SP-239, Kinetics and Thermodynamics in High Temperature Gases Conference, Lewis Research Center, Cleveland, Ohio, 1970. See also: S. Gordon and B.J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations", NASA, SP-273, 1971.

10. F. E. Spencer, and A. A. Orning, "An Algorithm for Calculating Multiphase Chemical Equilibrium", Bureau of Mines Report of Investigation, #7786, 1973.

11. W. D. Madeley and J. M. Toguri, "The Application of Free Energy Minimization to Determine Equilibrium Compositions in Systems of Metallurgical Interest, Canadian Metallurgical Quarterly, 12, p. 71, 1973.

12. F. van Zeggeren, and S. H. Storey, The Calculation of Chemical Equilibria, Cambridge Univ. Press, Cambridge, 1970.

13. M. Blander, "Computer Modeling of Gas-Condensed Phase Equilibria: Present Status and Some Future Needs in Science and Technology", 10th Material Research Symposium on Characterization of High Temperature Vapors and Gases, NBS Special Publication #561, Vol. 2, p. 1707, 1979.

14. E. Schnedler, Computer Modeling of High Temperature Lamp Chemistry, High Temperature Lamp Chemistry, Proc. of the Symposium on Science and Technology of High Temperature Light Sources, p. 95, Edited by: E. G. Zubler, GEC Nela Park, Cleveland, Ohio, Lib. Congress #85-70832, 1985.

Thermodynamic Data

15. JANAF Thermochemical Tables
Thermal Research, The Dow Chemical Company, Midland, Michigan 48640
See Also: J. Phys. Chem. Ref. Data volumes 3/74, 4/75, 7/78, and 11/82 for JANAF 1974, 1975, 1978, and 1982 Supplements

16. K. K. Kelley, Contributions To The Data on Theoretical Metallurgy, Bureau of Mines,:
Bulletin 406, VII: "The Thermodynamic Properties of Sulfur and its Inorganic Compounds," 1937.
Bulletin 584, XIII: "High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for Elements and Inorganic Compounds," 1960.
Bulletin 592, XIV: (with E. G. King)"Entropies of the Elements and Inorganic Compounds," 1961.

17. C. E. Wicks and F. E. Block, "Thermodynamic Properties of 65 Elements-Their Oxides, Halides, Carbides, and Nitrides," Bureau of Mines, Bulletin 605, 1963.

18. D. W. Scott, "Chemical Thermodynamic Properties of Hydrocarbons and Related Substances: Properties of the Akane Hydrocarbons, C1 Through C10, in the Ideal Gas State From 0 to 1500K." Bureau of Mines, Bulletin 666, 1974.

19. A. D. Mah and L. B. Pankratz, Contributions To The Data on Theoretical Metallurgy, Bureau of Mines, Bulletin 668, XVI. "Thermodynamic Properties of Nickel and its Inorganic Compounds," 1976.

20. L. B. Pankratz, Thermodynamic Properties of Halides, Bureau of Mines, Bulletin 674, 1984.

21. I. Barin, and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, New York, 1973 & 1977.

22. O. Kubaschewski, and C. B. Alcock, Metallurgical Thermochemistry, 5th Ed. Oxford (1979).

23. K. C. Mills, Thermodynamic Data for Inorganic Sulfides, Selenides, and Tellurides, Butterworth & Co., Ltd., London, England, 1974.

24. H. L. Schick, Thermodynamics of Certain Refactory Compounds, Vol. I, and Vol. II, Academic Press, New York, 1966.

25. D. D. Wagman et. al., Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, NBS Technical Notes: 3,4,5,6 and 7, 1968-1973.

26. D. D. Wagman, et. al., "Chemical Thermodynamic Properties of Compounds of Sodium, Potassium, and Rubidium: An Interim Tabulation of Selected Values", National Bureau of Standards, NBSIR 76-1034, 1976.

27. K. S. Krasnov, et. al., Handbook: Molecular Constants of Inorganic Compounds, [in Russian], Khimiya, 1968.

28. B. Rosen, Donnees Spectroscopiques Relatives aux Molecules Diatomiques, Pergamon Press, New York, 1970.

29. R. C. Feber, "Heats of Dissociation of Gaseous Halides", Los Alamos Scientific Laboratory, LA-3164, UC-4, Chemistry, TID-4500 (40th Ed.), 1964.

30. A. Glassner, "The Thermodynamical Properties of the Oxides, Fluorides, and Chlorides to 2500K", Argonne National Laboratory, ANL 5750, 1957.

31. Vedeneyev, et. al., Bond Energies, Ionization Potentials and Electron Affinities, St. Martins Press, New York, 1966.

32. G. V. Samsonov, The Oxide Handbook, IFI/Plenum, New York, Washington, Lond, 1973.

33. L. Kaufman, "Systems for Storage and Retrieval of Thermochemical Data and Calculation of Phase Diagrams", Manlabs, Inc., Cambridge, MA.

34. B. D. Smith, "Computer-Readable Data Bank Containing Thermodynamic Data on Pure Compounds," Thermodynamic Research Laboratory, Washington University, Saint Louis, Missouri 63130. See also NSRDS Reference Data Report, National Bureau of Standards, 4th quarter, 1980.

Auxiliary Chemical Data Programs

35. D. D. Wagman, R. H. Schumm and V. B. Parker, "A Computer-Assisted Evaluation of the Thermochemical Data of the Compounds of Thorium," National Bureau of Standards, NBSIR 77-1300, PB 273-171, 1977.

36. D. Garvin, V. B. Parker, D. D. Wagman and W. H. Evans, "A Combined Least Squares Approach to the Evaluation of Thermodynamic Data Networks," National Bureau of Standards, NBSIR 76-1147, 1976.

Transport Theory and Formulae

37. S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases, University Press, Cambridge, 1952.

38. R. S. Brokaw, "Thermal Conductivity of Gas Mixtures in Chemical Equilibrium II.," J. Chem. Phys. 32, pp. 1005-6, 1960.

39. J. M. Yos, Avco Technical Memorandum RAD-TM-63-7, AD 435053, 1963. (see also RAD-TR-65-7, 1965.)

40. R. S. Devoto, "Simplified Expressions for Transport Properties of Ionized Monoatomic Gases," Phys. of Fluids, 10, p. 2105, 1967.

41. C. Muckenfuss and C. F. Curtiss, "Thermal Conductivity of Multicomponent Gas Mixtures," J. Chem. Phys., 29, p. 1273, 1958.

42. L. S. Frost, "Conductivity of Seeded Atmospheric Pressure Plasma," J. App. Phys., 32, p. 2029, 1961.

43. W. L. Nighan, "Electrical Conductivity of Partially Ionized Noble Gases," Phys. of Fluids, 12, p. 162, 1969.

44. C. H. Kruger, M. Mitchner and V. Daybelge, AIAA J., 6, p. 1712, 1968.

45. R. S. Devoto, "Transport Coefficients of High Pressure Argon in a Magnetic Field," USAF ARL 71-0075, 1971.

46. L. Spitzer, Physics of Fully Ionized Gases, Interscience Publishers Inc., New York, p. 84, 1956.

Interaction Potentials

47. See ref. 1, p. 1164.-71

48. L. Monchick, "Collision Integrals for the Exponential Repulsive Potential," Phys. of Fluids, 2, p. 695, 1959.

49. L. Monchick and E. A. Mason, "Transport Properties of Polar Gases," J. Chem. Phys., 35, p. 1676, 1961.

50. F. J. Smith and J. Munn, "Automatic Calculation of the Transport Collision Integrals with Tables for the Morse Potential," J. Chem. Phys., 41, p. 3560, 1964.

51. E. A. Mason and R. J. Munn, "Transport Coefficients of Ionized Gases," Phys. of Fluids, 10, p. 1827, 1967.

52. T. Kihara, M. H. Taylor, and J. O. Hirschfelder, "Transport Properties for Gases Assuming Inverse Power Intermolecular Potentials," J. Chem. Phys., 3, p. 715, 1960.

53. See Ref. 1, p. 548.

54. J. W. Sheldon, "Mobility of Positive Ions in Their Own Gas: Determination of Average Momentum Transfer Cross Section", NASA TN-D-2408, Lewis Research Center, Cleveland, OH, 1964. See also: J. W. Sheldon and E. J. Mainista, "Atomic Beam Determination of the Cesium-Cesium Total Scattering Cross Section", Lewis Research Center, Cleveland, OH, NASA TN-D-3160, 1965.

Cross Section Data and/or Transport Related Calculations

55. L. J. Kieffer, "Bibliography of Low Energy Electron Collision Cross Section Data", National Bureau of Standards, Misc. Publication 289, 1967.

56. L. J. Kieffer, "A Compilation of Electron Collision Cross Section Data for Modeling Gas Discharge Lasers", JILA Information Center Report 13, Univ. Col., Boulder, CO, 1973.

57. G. W. Kaye and T. H. Laby, Tables of Physical and Chemical Constants, John Wiley and Sons, Inc., New York, p. 195, 1966.

58. S. C. Brown, Basic Data of Plasma Physics, MIT Press, Cambridge, MA, 1967.

59. J. L. Pack and A. V. Phelps, "Drift Velocities of Slow Electrons in Helium, Neon, Argon, Hydrogen and Nitrogen," Phys. Rev., 121, p. 798, 1961.

60. J. T. Vanderslice, S. Weissman, E. A. Mason, and R. J. Fallon, "High Temperature Transport Properties of Dissociating Hydrogen," Phys. of Fluids, 5, p. 155, 1962.

61. E. GerJuoy, "Atomic Scattering Processes," Rev. Modern Phys. 33, p. 544, 1961.

62. H. S. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena, Clarendon Press, Oxford, 1952.

63. K. S. Yun and E. A. Mason, "Collision Integrals for Transport Properties of Dissociating Air at High Temperatures," Phys. of Fluids, 5, p. 380, 1962.

64. R. S. Brokaw, "Alignment Charts for Transport Properties Viscosity, Thermal Conductivity, and Diffusion Coefficients for Nonpolar Gases and Gas Mixtures," NASA TR R-81, Lewis Research Center, Cleveland, OH, 1960.

65. R. S. Devoto, "Transport Coefficients of Partially Ionized Argon," Phys. of Fluids, 10, p. 354, 1967.

66. R. H. Davies, E. A. Mason, and R. J. Munn, "High-Temperature Transport Properties of Alkali Metal Vapors," Phys. of Fluids, 8, p. 444, 1965.

67. Rapp and W. E. Francis, "Charge Exchange Between Gaseous Ions and Atoms," J. Chem. Phys., 37, p. 2631-2645, 1962.

68. I. Popescu Iovitsu and N. Ionescu-Pallas, "Resonant Charge Exchange and Kinetics of Ions," Soviet Phys. - Tech. Phys., 4, p. 781, 1960.

69. Stebbings, B. R. Turner, and A. C. H. Smith, "Charge Transfer in Oxygen, Nitrogen and Nitric Oxide," J. Chem. Phys., 38, p. 2277, 1963.

70. V. B. Leonas and E. V. Samuilov, "Methods of Determining the Interaction Potentials of Atoms, Molecules and Ions," High Temperature, 4, p. 664-675, 1966.

71. R. S. Devoto, "Transport Coefficients of Partially Ionized Krypton, and Xenon," AIAA J., 7, p. 199, 1969.

72. R. S. Brokaw, "Recent Advances Concerning the Transport Properties of Dilute Gases," Int. J. Engng. Sci., 3, p. 251-267, Pergamon Press, 1965.

73. R. S. Devoto, "Transport Properties of Ionized Monatomic Gases," Phys. of Fluids, 9, p. 1230, 1966.

74. J. Physical and Chemical Reference Data, Published by Am. Chem. Soc. and Am. Inst. Phys. for NBS, Vol. 1/72 → 15/86.

THERMAL PLASMA RESEARCH AREAS

CHAPTER 9

MODELING

Session Chairman

M. Boulos
Chemical Engineering Department
Universite de Sherbrooke
Sherbrooke, Quebec, Canada J1K2R

P. Fauchais
Laboratory Thermodynamique
Universite de Limoges
87060 Limoges Cedex, France

9.1 EQUILIBRIUM AND NONEQUILIBRIUM CONSIDERATIONS IN MODELING

T. L. EDDY
Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Equilibrium Versus Nonequilibrium

Consider the Boltzmann integrodifferential transport equation which permits the evaluation of the molecular energy distribution function of the i^{th} type of particles, f_i [1]:

$$\frac{\partial f_i}{\partial t} + c_i \frac{\partial f_i}{\partial r} + F_i \frac{\partial f_i}{\partial c_i} = \sum_{j=1}^{r} \left[\Gamma_{ij}^{(+)} - \Gamma_{ij}^{(-)} \right] \tag{1}$$

where t is time, r is position, c_i is velocity, F_i is force/unit mass, and the Γ_{ij} net up-down collision integrals between i-type and j-type particles. The terms on the left represent transient, spacial gradient, and external body force effects on the distribution function f_i. The rhs represents the net effect of intermolecular collisions.

If the system being considered is isolated, then in sufficient time:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial r} = F_i = 0, \tag{2}$$

and we obtain the equilibrium solution via intermolecular collisions, which for thermal plasma densities and specific energies is the Maxwell velocity distribution and the Boltzmann energy distribution. Hence

Equilibrium ≡ Thermodynamic Equilibrium

for an isolated or infinite system. Thermodynamic Equilibrium (TE) includes Radiative Equilibrium which requires all frequencies to satisfy the Planck function and hence be optically thick.

In thermal plasmas, transients, gradients and external body forces are often relatively weak so that a quasi-equilibrium locally finite state occurs called Local Thermodynamic Equilibrium (abbreviated here as LTDE to distinguish it from Local Thermal Equilibrium - LTE). Radiative Equilibrium does not hold because some transitions will be optically-thin and/or partially thick, otherwise the distribution functions will be Maxwell-Boltzmann (MB). As a result, Local Thermal Equilibrium (LTE) with all temperatures $T_i = T_j = \ldots$, Local Mechanical Equilibrium (LME) with all pressures $p_i = p_j = \ldots$ (not <u>partial</u> pressures), Local Chemical Equilibrium (LChE) with all chemical potentials $\mu_i = \mu_j = \ldots$, and so on will occur.

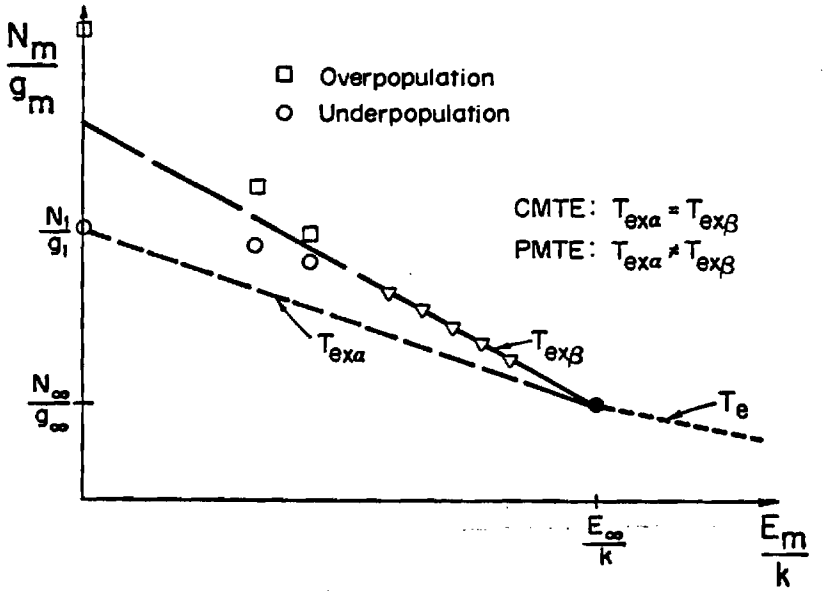


Fig. 1 Meaningful plasma temperatures:

- T_e ~ free electron translational temperature.
- T_g ~ atom, ion, or gas translational temperature.
- $T_{ex\beta}$ ~ upper level electronic excitation temperature.
- T_{exa} ~ total electronic excitation or Boltzmann temperature between m = 1 and m = ∞.

Nonequilibrium may occur when there are strong transient effects as in pulsed arcs, switching and afterglow; strong spacial effects as in plasma boundaries and with cold gas/particulate injection; and strong external body forces such as with magnetic or electric fields as found in cathode and anode fall regions. In low pressure plasmas, these effects alter the distribution function from the Equilibrium distribution and some non-MB distribution functions are used or the distribution function is treated as a variable function.

In high pressure plasmas, a MB distribution can usually be assumed because of the relatively small intermolecular relaxation times and mean free paths as well as the relatively stronger intermolecular forces. However, it is also experimentally found that different energy modes (translation, rotation, vibration, electronic, etc.) or species can have different distribution parameter values (e.g., $T_k \neq T_p$) within the same small local region, and that sometimes the energy mode follows the MB distribution over only part of the energy levels of the mode. This can be explained physically in terms of the ability of particular energy levels to equilibrate with each other or some other energy mode or species. To date, non-LTE is distinguished by different valued distribution parameters, but not non-LME or non-LChE. Chemical nonequilibria is usually handled with a "kinetic" method which assumes LTE, even though temperatures measured in reaction zones may vary between vibrational, rotational and translational energy modes. Future research should alleviate this paradox.

Description of Non-LTE Using f_{MB}

It has been shown for thermal plasmas near atmospheric pressure that the translational energy distribution is MB [2]. The electronic distribution functions may deviate from MB. Typical deviations will be discussed below in the discussion of selected non-LTE models.

Two-Temperature Models (2-T)

The 2-T models [3-5] usually assume that the electron (T_e) and heavy particle or gas (T_g) translational energy temperatures dominate as follows:

$$T_e = T_{exa} = T_{exi} = T_{ex\beta,a} = T_{ex\beta,i} \quad , \tag{3}$$

$$T_g = T_a = T_i = T_r = T_v \quad , \tag{4}$$

where (see Fig. 1) T_{exa}, T_{exi} are defined here as the Boltzmann temperatures between ground state and E_∞ (or E_I the lowered ionization potential) for the atom (a) and ion(i), respectively; $T_{ex\beta}$ is the ratio temperature of the highest excited levels; and T_r and T_v are the rotational and the vibrational excitation temperatures.

Typical equations for a 2-T model are given in Table I. The advantage of the model is that it adds only one variable (T_e) and hence one more equation, (the electron energy equation) to the LTE set of equations. Solutions can be obtained for fairly complex problems. The major disadvantages are that it may be too simple and that T_e and T_g values predicted are difficult to confirm. It is usually assumed via the Partial LTE (PLTE) model that $T_e = T_{ex\beta,a}$ however, diagnostic calculations using the PLTE ionization (Saha) equation have shown in general that [6]

$$T_{exa} \neq T_e \neq T_{ex\beta,a} \quad . \tag{5}$$

The saving grace of the 2-T models is that $T_{ex\beta}$ is usually not employed. The GMTE multitemperature model (discussed later) shows that chemical equilibrium is mainly a function of T_e (and T_g), though the population of excited levels is mainly a function of T_{exa}. Therefore, T_e and T_g are the most appropriate two temperatures, so models based on these temperatures should give good results for transport properties and modeling the conservation equations. Problems or apparent contradictions arise when excited levels related to T_{exa} or $T_{ex\beta}$ are used to determine T_e (erroneously) for comparison of models with experiment. This is only valid in LTE which is often nonexistant. Both T_e and T_g are very difficult to measure (see Ch. 7.2). The specification of these temperatures as boundary conditions is convenient but of questionable merit when one can not confirm the values.

Many of the conservation relations are not affected explicitly by variations between similar models. They are affected by density and temperature value changes. The densities are usually controlled by the form of the ionization equation, as well as the equation of state. Table II compares the 2-T ionization equation with others. A major limitation is the exclusion of radiative transfer which could possibly be included using the methods of Lowke [7].

Table I: 2-T Plasma Modeling Equations.

Quasi-neutrality: $N_e = N_i$

State: $p = N_e k T_e + (N_i + N_a)\, k T_g$

Chem/Ioniz: $\dfrac{N_e N_i}{N_a} = 2\,\dfrac{Z_{exi}[T_e]}{Z_{exa}[T_e]}\left[\dfrac{2\pi m_e k T_e}{h^2}\right]^{3/2} \exp\left[\dfrac{-E_\infty}{kT_e}\right]$

Mass: $\vec{\nabla} \cdot \rho\, \vec{u} = 0$

Momentum: $\rho \vec{u} \cdot \vec{\nabla}\, \vec{u} = -\vec{\nabla}\, p + \vec{\nabla} \cdot \mu\, \vec{\nabla}\, \vec{u} + \vec{J} \times \vec{B}$

Gas Energy: $\vec{\nabla} \cdot \left[\dfrac{5}{2}\, k\, (N_a + N_e) T_g\, \vec{u}\right] = \vec{\nabla} \cdot \lambda_g \vec{\nabla} T_g + \dfrac{3}{2}\, k \left(T_e - T_g\right) N_e \dfrac{2m_e}{m_g}\, \bar{\nu}_{eg}$

Electron Energy: $\vec{\nabla} \cdot \left[\dfrac{5}{2}\, kT_e + E_{\infty,a}\right] N_e\, \vec{u} =$

$$\vec{\nabla} \cdot \lambda_e \vec{\nabla} T_e - \frac{3}{2} k \left(T_e - T_g\right) N_e \frac{2m_e}{m_g}\, \vec{\nu}_{eg} + \sigma_e E^2 + Q_{RAD}$$

Maxwell: $\mathrm{ROT}\ \vec{H} = j$

$\mathrm{ROT}\ \vec{E} = -\mu_o\, \partial \vec{H}/\partial t$

$\mathrm{DIV}\ \vec{B} = 0$

Table II. Comparison of Ionization Equations.

2-T or 2-T KINETIC METHOD

$$\frac{N_e^2}{N_a} = 2\,\frac{Z_{exi}[T_e]}{Z_{exa}[T_e]}\left(\frac{2\pi m_e kT_e}{h^2}\right)^{3/2}\exp\left[\frac{-E_\infty}{kT_e}\right]$$

PLTE/LCRE

$$\frac{N_e^2}{N_m} = 2\,\frac{Z_{exi}[T_e]}{g_m}\left(\frac{2\pi m_e kT_e}{h^2}\right)^{3/2}\exp\left[\frac{-(E_\infty - E_m)}{kT_e}\right]$$

MSE:PRIGOGINE (1940)

$$N_e\left(\frac{N_i}{N_a}\right)^{T_g/T_e} = 2\left(\frac{Z_{exi}[T_g]}{Z_{exa}[T_g]}\right)^{T_g/T_e}\left(\frac{2\pi m_e kT_e}{h^2}\right)^{3/2}\exp\left(\frac{-E_\infty}{kT_e}\right)$$

MSE:POTAPOV (1966)

$$N_e\left(\frac{N_i}{N_a}\right)^{T_g/T_e} = 2\left(\frac{Z_{exi}[T_e]}{Z_{exa}[T_e]}\right)\left(\frac{2\pi m_e kT_e}{h^2}\right)^{3/2}\exp\left(\frac{-E_\infty}{kT_e}\right)$$

MTE: EDDY, ET AL. (1973)

$$\frac{N_e^2}{N_a} = 2\left(\frac{Z_{exi}[T_{exa}]}{Z_{exa}[T_{exa}]}\right)\left(\frac{2\pi m_e kT_e}{h^2}\right)^{3/2}\exp\left(\frac{-E_\infty}{kT_{exa}}\right)$$

GMTE: EDDY & CHO (1986)

$$N_e\left(\frac{N_i}{N_a}\right)^{T_g/T_e} = 2\left(\frac{Z_{exi}[T_{exa}]}{Z_{exa}[T_{exa}]}\right)^{\frac{T_{exa}}{T_e}}\left(\frac{2\pi m_e kT_e}{h^2}\right)^{3/2}\exp\left(\frac{-E_\infty}{kT_e}\right)$$

Partial-LTE(PLTE) and Local Collisional-Radiative Equilibrium(LCRE) Models

The Partial-LTE (PLTE) Models [3,8-10] assume that the highest excited levels are distributed according to the electron temperature:

$$T_{ex\beta,a} = T_e \neq T_g \quad . \tag{6}$$

The PLTE assumption is usually coupled with a Collisional-Radiative model in order to determine lower energy level populations and the atom density, because the ground state is either over- or underpopulated based on $T_e = T_{ex\beta}$. The PLTE/LCRE ionization equation is given in Table II.

The collisional-radiative model includes various up/down collisional and radiative processes to determine the deviation of electronic levels from a Boltzmann distribution at T_e. The deviation is expressed in terms of a departure coefficient b_m for level m based on the upper level ionization equation such that [3]

$$\left[\frac{N_e^2}{N_m}\right]_{ACTUAL} \equiv b_m \left[\frac{N_e^2}{N_m}\right]^* \quad , \tag{7}$$

where

$$\left[\frac{N_e^2}{N_m}\right]^* = 2\,\frac{Z_{exi}}{Z_{exa}} \left[\frac{2\pi m_e kT_e}{h^2}\right]^{3/2} \exp\left[\frac{-(E_I - E_m)}{kT_e}\right] \tag{8}$$

and * indicates the PLTE (or "equilibrium") expression with T_e and N_e as independent variables. The physical meaning of b_n is more obvious from [9,10]:

$$1/b_m = \varsigma_m \equiv N_m/N_m^*(T_e, N_e) \quad , \tag{9}$$

where $N_m^*(T_e,N_e)$ is obtained from (8). The behavior of b_m is

$$b_m \to 1 \text{ as } m \to \infty \quad , \quad \text{and} \quad b_m \geq \text{or} \leq 1 \text{ as } m \to 1. \tag{10}$$

The advantages of the PLTE/LCRE model is that the non-Boltzmann electronic energy level distribution can be determined and that calculations can even be made on a personal computer. The disadvantages are that LCRE, the model does not consider radiative transfer except as a specified self-absorption, e.g. via optically thick resonance lines [7] or specified Holstein escape factor values [3]. This can be relaxed with the non-local CRE model, which includes adiative transfer via variable radiation escape [11] or spectrally dependent radiative transfer [12]. A more serious disadvantage is that PLTE methods extrapolated to E_∞ or E_I [6] find $T_{exa} \neq T_e \neq T_{ex\beta,a}$ hence, the foundation of the model leading to the ionization equation used is questionable.

Non-Local Collisional-Radiative Equilibrium (non-LCRE) Models

These are considered separately from the PLTE/LCRE models because it is not necessary to use the PLTE constraint. The non-local aspect comes from the non-

local radiative transfer input through variable radiative escape factors [11] or spectrally dependent radiative transfer [12].

This category also includes collisional-radiative models which use the PLTE assumption at only very high lying levels so that measureable excited levels are not pre-determined [13,14]. The non-LCRE or CRE model is therefore, one of the best models available. Its limitations lie in the quality of the cross sections or rate constants available and the complexity of solution for multicomponent plasmas with arbitrary geometries.

Statistical Equilibrium and Radiative Transfer (SERT) Models

The SERT models parallel the development of LCRE and CRE models. The SERT models were the first to include radiative transfer seriously by writing the source function for a line (or continuum) [15, 16],

$$S_\nu = B_\nu \left[T_{ex}\right] = \frac{\int I_\nu \phi_\nu d_\nu + \epsilon B_\nu[T_e] + \theta}{1 + \epsilon + \Delta} \quad , \tag{11}$$

which is equal to the Planck function of an electronic excitation temperature, T_{ex}, in terms of the radiative field $\int I\phi d\nu$, collisional excitations $\epsilon B_\nu[Te]$ and de-excitation ϵ, collisional and radiative ionizations θ and recombination Δ, and radiative de-excitation 1, where all are normalized to the transition probability.

The advantages are similar to the non-LCRE models and include the capability to determine when $T_{ex} = T_e$ [6]. The disadvantages include the difficulties in solution over all significant frequencies which are further complicated with each additional level added to the multilevel atom solution.

Multitemperature Models

Most of the Multitemperature models are similar in that they are flexible as to the number of temperatures which may be used. The derivations are based on each subsystem k having its own temperature T_k. Prigogine [17] developed a MSE (Multitemperature Saha Equation) assuming each species had its own temperature:

$$T_a \neq T_e \neq T_i \ . \tag{12}$$

Potapov [18] developed a 2-T MSE based on T_e and T_g and equations (3) and (4), but obtained a different 2-T ionization equation than most 2-T models use, as shown in Table II. The $\theta_g = T_e/T_g$ powers can make tremendous differences between MSE and PLTE based 2-T species densities.

A Multithermal Equilibrium (MTE) model [19], based on experimental observations, extended the temperature identification to partial energy modes (see Fig. 1):

$$\text{Complete MTE(CMTE): } T_g \neq T_e \neq T_{ex\beta} = T_{exa}, \tag{13}$$

$$\text{Partial MTE(PMTE): } T_g \neq T_e \neq T_{ex\beta} \neq T_{exa}, \tag{14}$$

The MTE model has an ionization equation resembling the PLTE form as shown in Table II.

Recent work [20,21] has shown that the assumed equivalence of ensemble temperatures is an oversimplification, so that the MTE model is limited, like the PLTE model, to near-LTE situations. A generalized MTE (GMTE) model is also found to be a generalized extension of the MSE models and can be extended to the complete and partial energy modes (CMTE and PMTE) discussed above, whose concepts are still valid.

The general form of the law of mass action for the multitemperature models is [18]:

$$\prod_j N_j^{\eta_j kT_j} = e^{-\Sigma\eta_j E_{o,j}} \prod_j \left[Z_{t,j}^{\eta_j kT_{t,j}} \left(\prod_k^{int} Z_{k,j} \right)^{\eta_j kT_{k,j}} \right] , \qquad (15)$$

where η_j is the stoichiometric coefficient of species j, $E_{o,j}$ is the zero energy correction for partition function energies, and $Z_{t,j}$ is the translational partition function of species j. The k-product is over internal energy modes. From this equation, the various MSE, MTE and GMTE ionization equations can be written as in Table II. The PMTE relations are obtained by pivoting around the psuedo level density at E_∞ (or the lowered value E_I).

The advantage of the MSE and GMTE models is that the relations are rigorously derived from fundamental concepts and are based on experimental observations. They are flexible as to CMTE and PMTE and hence utilize physically meaningful temperatures in which the 2-T, PLTE, and CRE models can be expressed, including the b_n. The number of conservation equations must be increased to match the increase in temperature variables. This can be done by adding electronic excitation energy equations with collisional-radiative terms which can be evaluated as functions of the temperatures and species densities to facilitate solution [22]. Radiative transfer is included via radiation escape factors. The disadvantage is the additional complexity analogous to the CRE models.

Kinetic Methods

The kinetic method for determining species densities in plasmas [23] is a modified 2-T model which assumes that all reaction rates are functions of either T_e or T_g. The form for the reaction rate is

$$k_{f \text{ or } r} = C_1 T^{C_2} \exp(-C_3/kT), \qquad (16)$$

where k_f, k_r are the forward and reverse reaction rates and C_1, C_2, C_3 are constants obtained from experimental data. The measure of forward progress ξ of a reaction $\Sigma\eta_{fj}M_j \rightleftarrows \Sigma\eta_{rj}M_j$ is given by

$$\frac{d\xi}{dt} = \prod_j N_j^{\eta_{fj}} k_f - \prod_j N_j^{\eta_{rj}} k_r \quad . \qquad (17)$$

Steady state concentrations are then given by

$$\prod_j N_j^{\eta_j} = \frac{k_f}{k_r} = \exp\left[\frac{-\Delta E_o}{kT}\right] \prod_j Z_j^{\eta_j} \quad , \tag{18}$$

where the rhs is obtained only in LTE at T. A casual comparison of (18) and (15) suggests a contradiction; however, (18) is a rather simplistic expression and $k_{f,r}$ should also depend on the order of the reaction in which empirical consideration of species concentrations or densities enters. The view that kinetic methods are "pure" is somewhat of an illusion. Also the availability of reliable cross sections is the exception rather than the rule. More research needs to be done in this area.

A comparison [23] between values from Kinetic and MSE methods unfortunately misapplies the MSE method. When corrected, the two methods agree in steady state values at θ_g values considered ($\theta_g \sim 1.2 \rightarrow 1.4$). Aubreton [24] has compared the MSE method of Potapov [18] and a pseudo-kinetic method in the form of predicting non-LTE transport coefficients. The results are similar, but values at $\theta_g < 3$ differ by only 10-20%. In addition, the pseudo-kinetic method predicts that discontinuities appear at $\theta_g \gtrsim 3$ which is not the case with the MSE model. Similar discontinuities are found using GMTE diagnostic analyses with large θ_g.

Other kinetic methods use a collisional-radiative model in transient mode [25]. These models show that equilibrium of the ground state occurs at much, much longer times than the excited levels [26]. This result can greatly influence the modeling of circuit breakers and other transient plasma phenomena.

The advantages of the kinetic method are 1) in transient analyses involving relaxation processes and 2) in the convenient form of the non-LTE expression in (18). Many of the present 2-T applications neglect distributions of excited levels at other than T_e. It would be beneficial to look at multitemperature kinetic methods. A possible disadvantage of the kinetic method is that an ionization equation is replaced by an expression for which the reaction rates need to be determined from experiment or estimated. This may be an advantage in some complex plasma processes if the overall rates can be used, which would in most cases limit scaling or application to a different type of reactor.

Conclusion

The major questions that remain are what simplifications can be made in the ionization equation for a particular application to simplify the solution procedure and to resolve the application of a wide variety of ionization models and/or when do kinetic models need to be used. Future experimental work should include diagnostics to compare measured and diagnostically calculated electron and gas temperatures and both thermodynamic and transport property measurement to compare with theoretical calculations from various models.

Theoretical work should include property calculations or formulations via collisional-radiative features (to possibly express them as properties) and transport property calculations for other than 2-T models.

References

1. C. L. Tien and J. H. Leinhard, Statistical Thermodynamics, Revised Printing, Hemisphere Publ. Corp., Washington, D.C. (1979).

2. T. F. Morse, Phys. Fluids, 6, 1420 (1963).

3. M. Mitchner and C. H. Kruger, Jr., Partially Ionized Gases, Wiley-Interscience Publ., New York (1973).

4. A. V. Donskoi, V. M. Goldfarb and V. S. Klubuikin, Physics and Technology of Low Temperature Plasmas, S. V. Dresvin (Ed.), English translation by T. Cheron and H. V. Eckert, Iowa State Univ. Press, Ames, Ch. 8 (1977).

5. J. Mostaghimi, P. Proulx and M.I. Boulos, 7th Int. Conf. Plas. Chem., v. 3, 865-872 (1985) and Plas. Chem. Plas. Proc., 4 (3), 199-217 (1984).

6. T. L. Eddy, J. Quant. Spectrosc. Radiat. Transfer, 33 (3), 197-211 (1985).

7. J. J. Lowke, J. Appl. Phys., 41 (6), 2588-2600 (1970).

8. D. R. Bates, A. E. Kingston and R. W. P. McWhirter, Proc. Roy. Soc., Ser A, 267, 297 (1962) and 270, 155 (1962).

9. A. V. Potapov and L. E. Tsvetkova, Opt. Spectrosc., 38 (3), 253-255 (1975).

10. C. Park, J. Quant. Spectrosc. Radiat. Transfer, 22, 101-112 9 (1979).

11. R. J. Giannaris and F. P. Incropera, J. Quant. Spectrosc. Radiat. Transfer, 13, 167-181 (1973) and 13, 183-195 (1973).

12. J. P. Apruzese, D. C. Kepple, K. G. Whitney, J. Davis and D. Dustin, Phys. Rev. A, 24, 1001 (1981).

13. A. M. Gomes, J. Phys. D: Appl. Phys., 16, 357-378 (1983).

14. J. M. Anderson, "Collisional radiative recombination and net ionization in mercury vapor," General Electric Co., Tech. Inf. Series, No. 85 CRD 220 (1985).

15. R. N. Thomas and R. G. Athay, Physics of the Solar Chromosphere, Interscience, New York (1961).

16. R. N. Thomas, Nonequilibrium Thermodynamics, U. Colo. Press, Boulder, (1961).

17. I. Prigogine, Bull. Cl. Sc. Acad. R. Belg., 26, 53-63 (1940).

18. A. V. Potapov, High Temperature, 4, 48-51 (1966).

19. T. L. Eddy, E. Pfender, and E.R.G. Eckert, IEEE Trans. Plasma Sci., 1, 31-42 (1973).

20. T. L. Eddy, A. Sedghinasab, K. Y. Cho, R. Frierson, Radiative Properties in Non-LTE Plasmas, Final Report, NSF Grant CPE-8311325, 1987.

21. K. Y. Cho, Ph.D. thesis, Georgia Institute of Technology, Atlanta, in preparation.

22. D. W. Pruitt, "Heat transfer model for an arc plasma in multithermal equilibrium", M.S. Special Problem, Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta (1984).

23. E. Richley and D. T. Tuma, J. Appl. Phys., 53 (12), 8537-8542 (1982).

24. J. Aubreton, "Etude de properiétés thermodynamiques et de transport dans des plasmas thermiques à l'équilibre et hors d'équilibre thermodynamiques: Applications aux plasmas de mélange Ar-H_2 et Ar-O_2, Thèse d'Etat, Université de Limoges (1985).

25. C. G. Braun, D. A. Erwin and M. A. Gunderson, Submitted to Applied Physics Letters (1986).

26. J. Kunc, personal communication (1986).

9.2 ON COLLISIONAL-RADIATIVE MODELS FOR PLASMAS IN NON-EQUILIBRIUM

JOSEPH A. KUNC
Departments of Aerospace Engineering and Physics
University of Southern California
Los Angeles, California 90089-0192

The microscopic state of a plasma in nonequilibrium is defined if the densities of all particles (including excited species), their average energies, energy distribution functions and intensities of spectral lines produced in the plasma are known. The most detailed and powerful approach allowing to determine such a microscopic state is the collisional-radiative model [1] that summarizes contributions of all the plasma elementary collisional and radiative processes (ionization, recombination, dissociation, spontaneous emission, etc.) to the plasma properties. The efficiencies of these elementary processes depend on the number of plasma particles and photons and their energy properties. Therefore, a general formulation of the collisional-radiative model includes three coupled groups of equations (a fourth group, plasma flow equations, are needed for flowing plasma):

1. A set of rate equations for production of different particles in the plasma,
2. A set of Boltzmann kinetic equations (one for each kind of species) describing the particles energy distribution functions, and
3. The radiative transport equation describing the intensity of radiation propagating in the plasma.

These equations form a system of differential-integral-algebraic equations which are very difficult to solve; therefore, some simplifications to the general collisional-radiative model are necessary. The most common assumptions, often well-justified from application point of view, are:

1. The plasma is not flowing (then the flow equations can be eliminated).
2. The plasma is uniform and in steady state (then all equations concerning particle behavior are space- and time-independent.
3. The particle distribution functions are Maxwellian (then the Boltzmann equations can be eliminated).
4. The reabsorption of radiation is treated by using the Holstein concept of escape factors (then the radiative transport equation can be eliminated).

However, it should be emphasized that even with the above assumptions a solution of the collisional-radiative model is a difficult task often carrying serious uncertainties [2,3]. These uncertainties result mainly from a lack (or significant inaccuracy) of the cross sections for many collisional processes and from the difficulties in estimation of the escape factors which are constants expected to be sufficiently realistic representations for the reabsorption of radiation in the plasma.

An example of the results [2] (the production of electrons and the contribution of atom-atom inelastic collisions) obtained from the collisional-radiative model for two-temperature (the electron temperature T_e differs in general from the atom temperature T_a) atomic hydrogen, with all four assumptions given above, are shown in Figure 1. The dot-dash curve is the equilibrium or Saha

limit. The solid curve includes both electron-atom and atom-atom inelastic processes, whereas the dashed curve omits the contribution of atom-atom inelastic processes. It is seen that the latter significantly contribute to the ionization process producing N_e at low temperatures such as found in most commercial plasma processing.

Another example [3] is the deviation of the electron energy distribution from Maxwellian as a result of electron-impact inelastic processes with

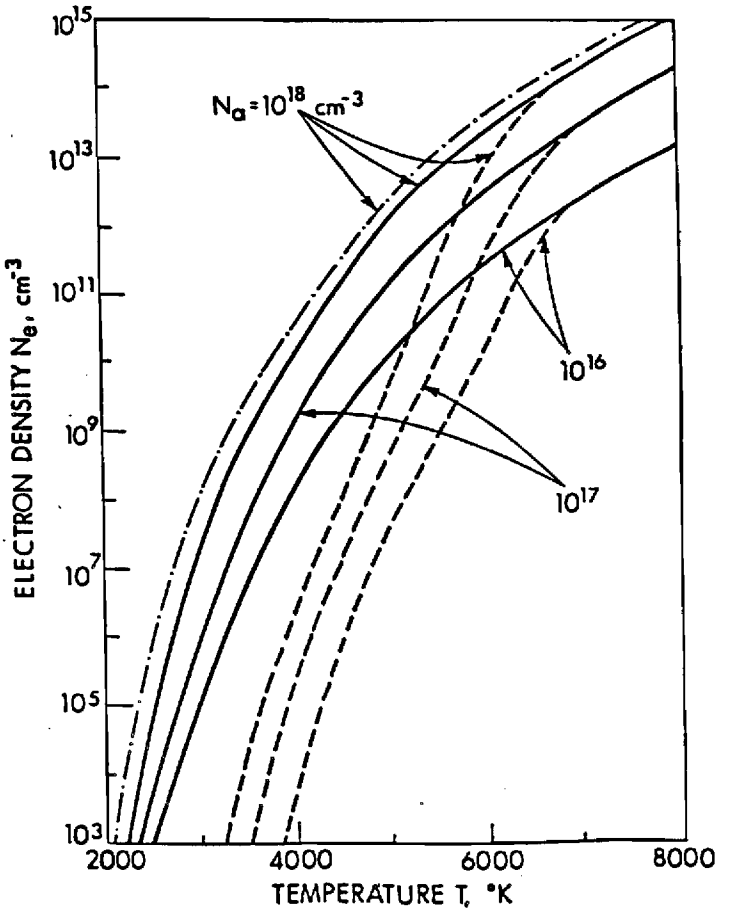


Figure 1. Electron density in steady-state atomic hydrogen plasma optically thick for Lyman series lines. N_a is the atom density. The electron and atom temperatures are taken as equal in this example ($T = T_e = T_a$). The curves are for the Saha or equilibrium limit (-.-), both electron-atom and atom-atom (---) or only electron-atom (---) inelastic processes.

subsequent escape of some radiation from the plasma. The solution of the collisional-radiative model for argon plasma, when assumption 3) given above is released, i.e. when the electron distribution function does not have to be Maxwellian, is shown in Figure 2. The ability for the electrons to collisionally ionize from the ground state is shown to rapidly diminish as the degree of ionization decreases below $x = 10^{-3}$.

The above remarks about the uncertainties of the collisional-radiative model and the difficulties in its solution (experiments able to verify properly the

theories have also presented some serious uncertainties [4-6]) suggest three major areas on which the theoretical work on the collisional-radiative plasma models should be concentrated:

a) More reliable measurements and theoretical calculations of the cross sections and transition probabilities for the collisional and radiative processes which are not well-described quantitatively and qualitatively. A good example of such processes are collisions involving excited particles.
b) Development of reliable approaches to the problem of transport of radiation in the plasmas.
c) Development of simplified collisional - radiative or 'thermodynamic' models of accuracy acceptable for various engineering applications. (This can be done successfully for specific types of plasmas or for specific applications.) Examples of such models are given in References [3] and [7].

It should be pointed out that the development of models described in item c) is of great importance for solving a variety of plasma related, engineering problems.

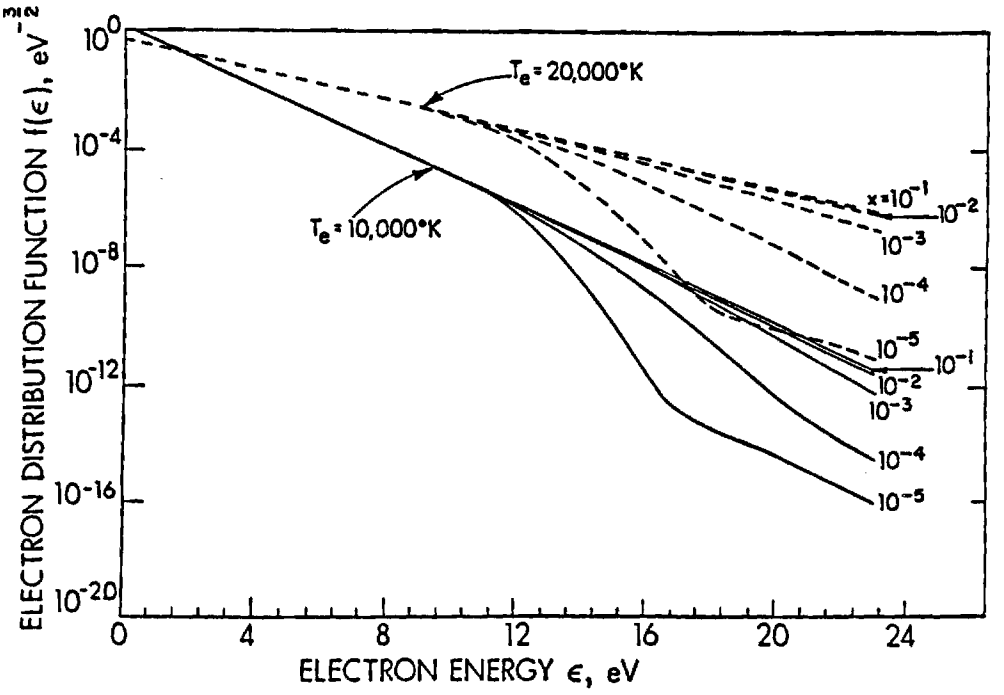


Figure 2. Electron distribution function in steady-state argon plasma. T_e and x are electron temperature and ionization degree, respectively. The pressure is 1 torr.

References

1. D.R. Bates, A.E. Kingston and R.W.P. McWhirter, Proc. Roy. Soc., A267, 297 (1962).

2. J.A. Kunc, Phys. Fluid, in press.

3. C. Braun and J.A. Kunc, Phys. Fluids, 30, 499 (1986).

4. D.D. Burgess, V.P. Myerscough, C.H. Skinner and J.M. Ward, J. Phys. B, 13, 1675 (1980).

5. R.W. Lee and W.L. Morgan, Phys. Rev., 32, 448 (1985).

6. T.L. Eddy, J. Quant. Spectrosc. Radiat. Transfer, 33, 197 (1985).

7. T.L. Eddy, E. Pfender, and E.R.G. Eckert, IEEE Trans. Plasma Sci., 1, 31 (1973).

9.3 TWO-TEMPERATURE TRANSPORT PROPERTIES

P. FAUCHAIS
Laboratoire Thermodynamique
Universite de Limoges
87060 Limoges Cedex, France

In a thermal plasma mode of particles with masses which are very different (heavy particles of mass m_h very high compared to the one of electrons m_e; $m_h \gg m_e$) relaxation towards an equilibrium value occurs in two stages in which characteristic times are very different [1]:

~ heavy particles as well as light ones relax separately towards two Maxwellian distributions respectively at T_e for the electrons and at T_h for the heavy particles. The corresponding relaxation times are rather short $\simeq \tau_1$

~ the two subsystems then relax much more slowly (with a characteristic time τ_2) towards thermal equilibrium.

This is due to the fact that the energy transfer through an elastic collision between an electron and a heavy particle is less efficient (in the ratio m_e/m_h) than the transfer between two particles with similar masses. It is of value to notice that during this relaxation, the energy distribution functions are not quite Maxwellian, but not perturbed enough to modify the analysis significantly [2].

Thermal equilibrium is then reached when τ_2 is short compared to the other characteristic times of the plasma (mechanical or residence time, diffusion, etc.)

In all cases to have equilibrium for the electrons among themselves at T_e, it is necessary that

$$\text{a)} \quad \langle \nu_{ee} \rangle \gg \sum_h \frac{m_e}{m_h} \langle \nu_{eh} \rangle$$

where $\langle \nu_{ee} \rangle$ and $\langle \nu_{eh} \rangle$ are the respective mean elastic collision frequencies and

$$\text{b)} \quad \langle \nu_{ee} \rangle \gg \langle \nu_{eh}(\text{NE}) \rangle$$

where $\langle \nu_{eh}(\text{NE}) \rangle$ is a nonelastic mean collision frequency.

The two conditions a and b are generally fulfilled when $n_e > 10^{18} - 10^{19}$ electrons/m^3 [3], i.e. in the core of thermal plasmas where the pressure is higher than about 100 torr.

A similar condition can be written for the heavy particles to be at equilibrium among themselves:

$$\langle \nu_{hh} \rangle \gg \langle \nu(\text{NE}) \rangle \ ,$$

which is a condition that is generally always fulfilled.

However, in the jet fringes, in the regions close to the wall, or where a cold gas is injected, the plasma is no longer in equilibrium and $T_e > T_h$ and the questions are how to calculate its properties and how to measure these nonequilibrium conditions.

From an experimental point of view: the heavy particle temperature is equal to the rotational temperature (collisional relaxation time between rotational states is short), the excitation temperature (measured from atomic lines) is usually smaller than the electron temperature except maybe for the excitation states close to the ionization limit. Thus the determination of the value of $\theta=T_e/T_h$ is not straightforward.

Assuming that $\theta=T_e/T_h$ is known, it is then possible to calculate the composition of the plasma through two methods: the Modified Saha Equation (MSE) or the kinetic approach. In the MSE method, the partition functions of the atoms (except for translation) are calculated at T_e while the partition functions of molecules are calculated at T_h. Writing the conservation of species and pressure, modified mass action laws are obtained [4], similar to those at equilibrium except for $1/\theta$ exponents for some terms. The main advantage of MSE is that it allows the use of all of the data gathered at equilibrium. However, for values of θ higher than 3, its use is questionable.

The kinetic approach (as for example the one developed by Richley [5]) consists of writing all the different reactions with their rate coefficients (direct and reverse) until a stationary state is reached when the number densities of the different species do not vary any more with time. One solves the corresponding equations including, if necessary, convection and diffusion terms. Besides the stiffness of the solutions (a problem that can be solved using predictor-corrector methods), the main problem is the lack of data for the reaction rates k_d or k_r which can be calculated through the collision cross sections assuming Maxwellian distributions and taking into account that the ratio k_d/k_r is equal to the equilibrium constant. To calculate the reaction rates, the electron temperature is to be used for the reactions of the type

$$M + e + X \overset{k}{\leftrightarrows} M + \text{Products}$$

while T_h is to be used for

$$M + X + Y \overset{k}{\leftrightarrows} M + \text{Products}.$$

The results depend strongly on the reactions taken into account and on the reaction rate coefficient values. As shown for example by Aubreton [6] for the Ar-H_2 mixture, the results obtained with the two methods are in good agreement up to $\theta=2$, slight divergences occur for θ between 2 and 3, and for $\theta > 3$ the reactions of the type $H_2+e \rightarrow 2H+e$, neglected in the MSE method, become important, which drastically increases the differences between the two methods.

Once the plasma composition is known, the transport properties can be calculated. For the elastic collisions (translational transport properties) the set of Boltzmann's equations is split in two [7], on one hand, the electron equation and on the other, the heavy particle equation. For the chemical

reactions such as dissociations, ionizations, ..., the reactive thermal conductivity K_R depends on diffusion. Bonnefoi [8] has recently introduced new diffusion forces allowing one to calculate K_R through a new approach, close to the one of Butler and Brokaw [9], but developed specially for two-temperature plasmas. Within the framework of this two-temperature model, the transport properties can be calculated as functions of the classical collision integrals, provided of course that the nonequilibrium is not too far from equilibrium, i.e., for $\theta \leq 3$. For completely out of equilibrium plasmas a new theory of transport properties should be developed, for example through the approach of Grad [1]. However, it is important to remember that the main problem is probably still the lack of data. The interaction potentials are known only for some plasma gases: Ar, He, H_2, N_2, O_2 and their mixtures but unknown when carbon, chlorine, metal, or oxide vapors are present as in most cases of plasma chemical reactions.

Of course when the data are available to calculate composition and transport properties as a function of T_e and T_h, the flow equations can be solved, as it has been shown for example by Chen [10] assuming laminar flow with two temperatures. In this case, the energy equation is split into two equations, one for the electrons and the other for the heavy species. The closure equation is obtained by calculating the energy exchange between electrons and heavy species through elastic collisions. However, up to now, such an approach has been developed only for the nonequilibrium due to the introduction of cold argon in an argon plasma and due to the differences of gathering the data (specifically transport properties). No attempt has been made for more complex plasmas containing diatomic molecules, for example. The results obtained with argon have emphasized the nonequilibrium effects induced by this cold gas injection specifically in the plasma jet fringes and near the walls. However, it is not actually possible to simultaneously calculate the flow and the kinetic reactions occurring in a simple case such as the introduction of cold oxygen into a nitrogen dc plasma jet. The only possibility is, for example, to assume no perturbation of the nitrogen plasma flow, a given trajectory for the cold injected oxygen, resulting in a temperature history $T(t)$ of the N_2-O_2 mixture along this trajectory and to calculate the evolution of the kinetic reactions with $T(t)$ [11].

If the flow is supposed to be turbulent, the problem is even more complex and questions such as what fraction of the total energy represents the turbulent energy for electrons and heavy species have no answers at the moment.

Finally, nonequilibrium calculations in the boundary layer of solid particles evaporating in a plasma flow are purely speculative at the moment. The calculations in an equilibrium model are still impossible when the modifications of the transport properties of the plasma caused by the vapor cannot be taken into account.

References

1. Grad H., "Theory of rarefied gases," Rarefied Gas Dynamics, Ed. by F. Devienne, Pergamon Press Inc., London (1960).

2. T. F. Morse, Phys. Fluids, 6, 1420 (1963).

3. C. A. Borghi, A. Veekkind and J. M. Wetzer, Physica, 121C, 269 (1983).

4. A. V. Potapov, "Chemical equilibrium of multitemperature systems," High Temp. 4, 48-51 (1966).

5. E. Richley and D. T. Tuma, "On the determination of particle concentrations in multitemperature plasma," J. Appl. Phys., 53 (12) 8537-8542 (1982).

6. J. Aubreton, "Etude de propriétés thermodynamiques et de transport dans les plasmas thermiques à l'equilibre et hors équilibre thermodynamiques: application aux plasmas de mélange Ar-H_2 et Ar-O_2", Thèse d'Etat, Université de Limoges, (1985).

7. R. S. Devoto, "Transport properties of ionized monatomic gases", Phys. Fluids, 9 (6), 1230-1239 (1966).

8. C. Bonnefoi, "Contribution au calcul des properiétés de transport d'un plasma à deux temperatures", Thèse d'Etat, Université de Limoges, (1983).

9. J. H. Butler and R. S. Brokaw, J. Chem. Phys., 26, 1636 (1957) and R. S. Brokaw, J. Chem. Phys., 32, 1005 (1960).

10. D. M. Chen, K. C. Hsu, and E. Pfender, "Two-temperature modeling of an arc plasma", Plasma Chem. and Plasma Proc., 1 (3) 295-314 (1981).

11. J. F. Coudert, "Contribution à la modelisation de la cinétique dans un plasma N_2-O_2 produit par un générateur à arc soufflé. Etude expérimentale de la repartition des temperatures dans l'ecoulemnt plasma soumis àl'injection d'un gaz froid", Thèse d'Etat, Université de Limoges (1986).

9.4 FLOW MODELING UNDER PLASMA CONDITIONS

MAHER I. BOULOS
Department of Chemical Engineering
University of Sherbrooke
Sherbrooke, Quebec, J1K 2R1

Introduction

Considerable progress has been achieved over the last ten years in the area of flow modeling under plasma conditions. For a number of reasons, these have not been always accompanied by validation of the mathematical models against experimental data. In this note, a brief summary of the principal achievements in flow modeling under plasma conditions is given together with suggestions for possible research needs.

Present Flow Modeling Capabilities

Most of the published flow modeling work under plasma conditions has been concerned with the calculation of the flow, temperature and concentration fields in the device under study through the numerical solution of the corresponding continuity, momentum, energy and mass transfer equations together with the electromagnetic field equations, whenever applicable.

Most of the work has been carried out for d.c. plasma jets, free burning and confined arcs, and r.f. inductively coupled discharges.

The principal assumptions used are:

a) One- or two-dimensional axisymetric flows under steady state conditions. Little attention has been given to the modeling of the transient behavior of arcs and discharges, or to three-dimensional flow problems, such as in the case of injection of a side jet into a principal plasma jet.

b) Both laminar and turbulent plasma flows have been studied although, by far, the great majority of flow modeling work has been limited to laminar flow conditions.

c) The large majority of flow modeling studies have been assuming local thermodynamic equilibrium (LTE). In a few cases such as in arcs and r.f. inductively coupled discharges non-LTE, two-temperature models have also been developed.

d) The assumption that the plasma is optically thin, has been largely adopted throughout the modeling literature with radiation losses treated as a volumetric heat sink. For most practical situations this assumption is reasonably valid because of the relatively small physical dimensions of the plasmas studied.

e) The importance of accounting for the variations of the thermodynamic and transport properties of the plasma with temperature has been recognized in the early stages and is fully incorporated in all of the modeling work. It should be noted, however, that due to the limited availability of reliable property data as a function of temperature for pure gases and their mixtures, by far the great majority of modeling work has been carried out for argon or nitrogen

as the plasma gas with considerably less attention given to the flow modeling of plasmas of mixed gases.

Areas Where a Specific Research Effort is Needed

- The development of appropriate turbulent models. Often one of the difficulties encountered in the modeling of flows under plasma conditions is the simultaneous presence of both laminar and turbulent flow regimes in the same flow field. This is largely due to the presence of steep temperature gradients resulting in the substantial variations of the viscosity of the plasma across the flow.

- The development of appropriate three-dimensional models for complex flow configurations such as the interaction of an oblique jet with a plasma stream. This configuration has important bearing on the mixing pattern achieved in a plasma reactor.

- The development of appropriate chemical kinetic models. These are necessary for the incorporation of the chemical transformations in the modeling of plasma reactors.

- The eventual development of appropriate models for the nucleation and growth processes could have an important impact on our ability to model the behavior of plasma reactors used for the synthesis of ultra fine powders.

- The computation, and the improved accessibility, to data banks for the thermodynamic and transport properties of pure gases and their mixtures under plasma conditions, over the temperature range 1000-30,000 K, under atmospheric pressure and soft vacuum conditions (50-760 torr).

- Last, but not least, is the availability of appropriate experimental data for model validation.

9.5 TURBULENCE IN PLASMAS

DAVID M. BENENSON
Department of Electrical and Computer Engineering
State University of New York at Buffalo
Buffalo, New York 14260

One principal objective of plasma research is to model a plasma system, conduct sufficiently detailed diagnostic experiments so as to establish the validity of the model and its associated assumptions, and, then, to successfully apply the model to practical cases and configurations. In these instances, one needs to predict and measure (locally) all dependent variables of interest, such as the flow and temperature fields, electric field, pressure, and number density. With particulate matter present, time and space resolved measurements of the particle velocity, temperature, and size are required.

As complex as are modeling and diagnostics for laminar plasma flows, much greater difficulties occur with the onset of turbulence. As with cold (i.e., nonelectrically conducting) flows, many plasma applications involve turbulence, e.g., plasma processing and circuit interruption. [In these cases, of course, laminar flow may be found over a portion of the plasma.]

Analytical studies of (fluid-mechanically) turbulent plasmas seem relatively few in number. These treat turbulence from several perspectives - such as through the basic conservation equations and their moments [1-5]; selected equations employed so as to focus on more specific aspects (e.g., electric field and electron density) [5,6]; the two-equation turbulence model (k-ϵ) [7-9]; and phenomenological approaches (e.g., mixing-length theories) [3, 10]. Experimental verification is limited, [5,7, 9-17] in respect to test configurations (e.g., cylindrical channel, converging-diverging nozzle), test media (e.g., argon, nitrogen, sulfur hexafluoride), flow rates, and diagnostics employed (e.g., electric field, temperature, velocity, pressure).

Diagnostics of the turbulent plasma become much more complex than those of cold turbulent or laminar plasma flows owing to difficulties in accessibility, interactions between the plasma and flow, and motions of the plasma column. Spectroscopic methods for determining temperature distributions and their (mean square) fluctuations have been proposed using multiple azimuthal observations [18]; approximations to this approach have been developed and applied [13,15]. Velocity and its fluctuations have been obtained principally through laser velocimetry and variants [9, 14, 16]; the effects of column motion have been included through the development and application of a scanning probe volume [17].

Recommendations for basic studies of turbulent plasmas include: (1) modeling - (a) application of a variety of approaches (e.g., basic equations, k-ϵ equations, phenomenological theories) to selected basic (or reference) configurations and (b) their application to candidate "real" configurations to further test the model validity, to compare the various analytical approaches employed, and to compare theory with experimental results; (2) experiment - (a) development of a library of coefficients or parameters that characterize the flow for a range of basic configurations (e.g., cylindrical channels, nozzles, jets) - in the same spirit as in cold flow [19] and, (b) using various basic configurations, determine all dependent variables of interest (temperature, velocity, etc.) over a wide range of flow rates, pressure, gases (in part, a quantitative extension of [20]) and use these results to guide in formulation of

theoretical models' [3] diagnostics - (a) determine the local mean and mean square fluctuations of all dependent variables of interest (temperature, flow field, etc.), with and without particulates present in the plasma and (b) determine, for the particulates in the plasma, the time and space resolved particle size, velocity, and temperature in plasmas of known (and controllable) turbulence levels.

References

1. G.S. Argyropoulos, S.T. Demetriades, and K. Lackner, "Compressible Turbulent Magnetohydrodynamic Boundary Layers," The Physics of Fluids, Vol. 11, pp. 2559-2566, 1968.

2. I.P. Shkarofsky, "Transport Effects in a Turbulent Flowing Plasma. The Moment Relations," Plasma Physics, Vol. 15, pp. 599-609, 1973.

3. I.P. Shkarofsky, "Analysis of Turbulent Flow in Wall-Stabilized Arc Discharges," Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, Report ARL 73-0133, 1973.

4. W.W. Bower and F.R. Incropera, "A Procedure for Turbulent Arc Calculations," Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, Report ARL 73-0038, 1973.

5. W.W. Bower and F.R. Incropera, "Turbulent Flow Predictions for the Argon Cascade Arc," Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, Report ARL 73-0039, 1973.

6. A. Demetriades and R. Grabow, "Mean and Fluctuating Electron Density in Equilibrium Turbulent Boundary Layers," AIAA Journal, Vol. 9, pp. 1533-1538, 1971.

7. N. El-Kaddah, J. McKelliget, and J. Szekely, "Heat Transfer and Fluid Flow in Plasma Spraying," Metallurgical Transactions, Vol. 15B, pp. 59-70, 1984.

8. E. Pfender and Y.C. Lee, "Particle Dynamics and Particle Heat and Mass Transfer in Thermal Plasmas. Part I. The Motion of a Single Particle without Thermal Effects," Plasma Chemistry and Plasma Processing, Vol. 5, pp. 211-237, 1985.

9. J. McKelliget, J. Szekely, M. Vardelle, and P. Fauchais, "Temperature and Velocity Fields in a Gas Stream Exiting a Plasma Torch. A Mathematical Model and its Experimental Verification," Plasma Chemistry and Plasma Processing, Vol. 2, pp. 317-332, 1982.

10. W. Hermann, U. Kogelschatz, L. Niemeyer, K. Ragaller, and E. Schade, "Investigation of the Physical Phenomena around Current Zero in HV Gas Blast Breakers," IEEE Transactions on Power Apparatus and Systems, Vol. PAS-95, pp. 1165-1176, 1976.

11. R.J. Hill and G.R. Jones, "The Influence of Laminar and Turbulent Flows upon the Electrical Characteristics of Wall-Stabilized Arcs," Journal of Physics D: Applied Physics, Vol. 12, pp. 1707-1720, 1979.

12. P.W. Runstadler, "The Laminar and Turbulent Flow of an Argon Arc Plasma," AIAA Plasmadynamics Conference, Monterey, California, Paper No. 66-189, 1966.

13. Y.K. Chien and D.M. Benenson, "Temperature Diagnostics in Turbulent Arcs," IEEE Transactions on Plasma Science, Vol. PS-8, pp. 411-417, 1980.

14. A. Vardelle, J.M. Baronnet, M. Vardelle, and P. Fauchais, "Measurements of the Plasma and Condensed Particles Parameters in a DC Plasma Jet," IEEE Transactions on Plasma Science, Vol. PS-8, pp. 417-424, 1980.

15. U. Sen and D.M. Benenson, "Temperature Measurements of a Dynamic, Turbulent Nitrogen Arc in High Speed Flow," Bulletin of the American Physical Society, Vol. 26, p. 162, 1986.

16. J. Lesinski, R. Gagne, and M.I. Boulos, "Gas and Particle Velocity Measurements in an Induction Plasma," 5th International Symposium on Plasma Chemistry, Edinburgh, Scotland, pp. 534-538, 1981.

17. D. Celenti and D.M. Benenson, "Measurements of Velocity in Laminar and Turbulent Arc Flows," Proceedings of the 34th Canadian Chemical Engineering Conference, Quebec City, Quebec, Canada, pp. 32-35, 1984.

18. P.W. Schreiber and A.M. Hunter, III, "Diagnostic Technique for Determining Local Properties of Turbulent Plasma", "Proceedings of the Xth International Conference on Phenomena in Ionized Gases," Oxford, Great Britain, p. 471, 1971.

19. H. Schlichting, Boundary Layer Theory, McGraw-Hill, New York, New York, 1960.

20. G. Frind and B.L. Damsky, "Electric Arcs in Turbulent Flows, III," Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, Report ARL 68-0067, 1968.

9.6 PLASMA-PARTICULATE MODELING

E. PFENDER
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Some of the most important processes in thermal plasma technology today require the injection of particulates (fine particles) into the plasma (plasma spraying, synthesis, decomposition, spheroidization, etc.). For the control and optimization of these processes it is necessary to have an understanding of the relative importance of various effects which influence the motion as well as heat and mass transfer of particulates injected into a thermal plasma. A series of recent review papers [1-4] which include many pertinent references, attempt an assessment of the relative importance of various affects which control the behavior of particulates in thermal plasmas.

Compared to the motion of particulates in ordinary gases, correction terms have to be introduced to account for the strongly varying properties in plasmas, for noncontinuum effects if small particles (<10 μm) are involved, for the Basset history term if relatively large and light particles are considered over long processing distances, and for thermophoresis under certain conditions [1, 2].

Heat and mass transfer may be affected by unsteady conditions, by modified convective heat transfer due to strongly varying plasma properties, by radiation and by internal conduction. In addition, particle shape, vaporization and evaporation, noncontinuum conditions, and particle charging may influence heat and mass transfer [3]. Some of these effects are still poorly understood and, therefore, it is not surprising to find poor agreement among the heat transfer relationships available in the literature [5].

Most of the previously published work refers to the behavior of single particles in plasmas or to very small particle loading conditions. At higher loading rates, coupling effects have to be considered [4] which are extremely important for actual applications. Unfortunately, very little is known about these coupling effects.

References

1. E. Pfender, "Heat and momentum transfer to particles in thermal plasma flows," Pure & Appl. Chem., 1179 (1985).

2. E. Pfender and Y.C. Lee, "Particle Dynamics and Particle Heat and Mass Transfer in Thermal Plasmas. I: The Motion of a Single Particle without Thermal Effects," Plasma Chem. and Plasma Proc., 5 (3), 211 (1985).

3. Y.C. Lee, Y.P. Chyou, and E. Pfender, "Particle Dynamics and Particle Heat and Mass Transfer in Thermal Plasmas. II: Particle Heat and Mass Transfer in Thermal Plasmas," Plasma Chem. and Plasma Proc., 5 (4), 391 (1985).

4. Y.C. Lee and E. Pfender, "Particle Dynamics and Particle Heat and Mass Transfer in Thermal Plasmas. III: Thermal Plasma Jet Reactors and Multiparticle Injection," Plasma Chem. and Plasma Proc., 7 (1), 1 (1987).

5. R.M. Young and E. Pfender, "Nusselt Number Correlations for Heat Transfer to Small Spheres in Thermal Plasma Flows," to be published in Plasma Chem. and Plasma Proc., 7 (2), 1987.

Luncheon group. Left to right: M. Boulos, D. Miller, N. Barcza, J. Heberlein and R. Goulard.

Luncheon group. Left to right: T. Meyer, E. Pfender, M. Venugopalan, S. Girshick, R. Libermann, D. Neushütz, and D. Benenson.

THERMAL PLASMA RESEARCH AREAS

CHAPTER 10

PLASMA-SOLID BOUNDARIES

Session Chairman

E. Pfender
Mechanical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

10.1 PLASMA-SOLID BOUNDARIES: OVERVIEW

E. PFENDER
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

The following brief review of plasma-solid boundaries will be restricted to boundaries between solid surfaces and thermal plasmas, i.e. the thermodynamic state of the plasma outside the boundary layer shall approach local thermodynamic equilibrium (LTE).

This situation is experienced in many thermal plasma applications as, for example, in confined high intensity arcs, in thermal r.f. discharges, and in confined plasma jets. It also includes the interface between an arc plasma and an electrode surface as well as the boundaries between the surfaces of small particles and surrounding plasmas. The latter situation is experienced during the initial phase of particle injection into a plasma (plasma spraying, plasma densification, plasma spheroidization, plasma decomposition, plasma synthesis, etc.)

According to the previously mentioned situations, plasma-solid boundaries may be classified in terms of the surfaces involved as

(1) surfaces on floating potential (no net current flow to the surface);
(2) biased surfaces (surfaces which draw net currents);
(3) electrodes (surfaces drawing the total current which sustains the plasma).

In addition, plasma bordering such surfaces may be classified as

(a) "active" (current-carrying) plasmas, and
(b) "passive" (field-free) plasmas.

Arcs, for example, fall into the first category, whereas plasma jets fall in the second category. This distinction is important, because an "active" plasma responds differently to the presence of a cold wall than a "passive" plasma.

Surfaces on Floating Potential

It is well known in convectional heat transfer that the properties of the boundary layer are crucial for determining heat transfer. The same is true for the interface between a plasma and a solid surface which may also be considered as a boundary layer [1]. The situation in the case of a plasma boundary layer is, however, much more complex for several reasons.

First of all, the presence of electric charges in the plasma gives rise to the formation of a sheath at the bottom of the boundary layer overlying the solid surface. The thickness of this sheath is in the order of 1-10 Debye lengths which, in turn, depends on electron densities and temperatures close to the surface [1,2]. The sheath in which deviations from quasi-neutrality occur may be considered as an electrical boundary layer accommodating the transition from the plasma to the solid surface. The presence of space charges in the sheath produces relatively large electric fields. Since the sheath is usually much thinner than the boundary layer, the effect of the sheath on heat conduction is neglected [1],

but the high electric fields in the sheath may affect the flux of charged particles across the boundary layer.

Secondly, the temperature variation across the boundary layer may exceed 10^4 K which imposes serious problems in terms of the determination of properties. It is customary today to use an integral average for all the properties [3,4],

$$\phi = \frac{1}{T_\infty - T_W} \int_{T_W}^{T_\infty} \phi \, dT ,$$

where ϕ stands for any property; T_W: surface temperature, T_∞: plasma temperature.

Related to the previously discussed problems are the extremely steep gradients of temperature ($> 10^6$ C/cm) and particle densities across the boundary layer which represent driving forces for corresponding fluxes. Fluxes of charged particles are due to ambipolar diffusion. Because of the rapid diffusions of such particles across the boundary layer, chemical reactions (for example recombination) may be too slow for establishing chemical equilibrium in the boundary layer, i.e. the boundary layer may be in a chemically "frozen" state. This has important consequences on the thermal conductivity (higher concentration of free electrons) which, in turn, enhances heat transfer by conduction [1,5]. In addition, ion pairs will arrive in this situation at the surface at a higher rate and by releasing their ionization energy upon recombination, heat transfer may be substantially enhanced [6]. This process is known as diffusion of ionization energy to the surface. Similar considerations apply to plasmas which contain molecular species. The temperature variation across the boundary layer establishes corresponding concentration gradients of atomic and molecular species leading to diffusion of dissociation energy to the surface.

Besides the previously mentioned deviation from chemical equilibrium in the boundary layer, there also may be substantial deviations from kinetic equilibrium, i.e. $T_e > T_h$ (T_e: electron temperature, T_h: heavy particle temperature) which imposes another complexity on boundary layer analysis [7-10]. These deviations are in general due to the poor energy exchange by elastic collisions of electrons with heavy particles in the plasma.

In the context of small solid particle injection into a thermal plasma, another complication is experienced. The Knudsen number based on the particle size may reach values $Kn > 10^{-2}$ which requires modifications of the continuum description of the boundary layer [11]. Heat transfer in this situation may be substantially reduced compared to heat transfer under continuum conditions.

It should also be mentioned that the properties of the surface itself (catalytic or noncatalytic) may affect conditions in the boundary layer and, therefore, may alter heat transfer [1,6].

Biased Surfaces

Boundary layers on biased surfaces may be treated similarly as those on floating potential. But due to the imposed biasing potential, there will be a net current flow crossing the boundary layer. This current which is assumed to be much less than the current required for sustaining the plasma, may enhance heat

transfer to the surface [6,12]. This situation is, for example, experienced with electric probes immersed into a plasma.

Electrodes

The solid-plasma boundary is strongly affected by the electric current passing through the boundary layer. The relatively high field strengths in front of the electrodes (cathode and anode fall) give rise to strong deviations from kinetic equilibrium ($T_e \gg T_h$) in addition to deviations from chemical equilibrium caused by steep gradients.

Studies of the anode boundary layer in high intensity argon arcs show that the electron temperature remains above 8,000K throughout the boundary layer whereas the heavy particle temperature drops to the temperature of the anode surface which may be close to room temperature [13]. Because of the steep gradients in front of the anode, the anode fall may assume negative values, a result which can only be understood by considering the generalized Ohm's law, i.e.

$$j = \sigma_e \text{ (E + terms due to gradients)}$$

where j : current density, σ_e: electrical conductivity and E : electric field strength.

The requirement of div $\vec{j}$ = 0 can only be met in the presence of steep gradients when $E < 0$, i.e. the anode fall becomes negative [13,14]. This result is important for establishing a valid anode heat transfer model.

The interaction of electric, magnetic, thermal, and fluid-dynamic effects in front of the cathode of a high-intensity arc makes the analysis of the boundary layer rather difficult. Results of recent analytical studies, including a review of previous work are given in Reference [15].

References

1. E.R.G. Eckert and E. Pfender, "Advances in Plasma Heat Transfer," Advances in Heat Transfer, Vol. 4, Academic Press, New York (1967).

2. M. Mitchner and C.H. Kruger, Jr., Partially Ionized Gases, John Wiley and Sons, New York, 1973.

3. E. Bourdin, P. Fauchais, and M. Boulos, Int. J. Heat Mass Transfer, 26, 567 (1983).

4. Y.C. Lee, Y.P. Chyou, and E. Pfender, Plasma Chem. and Plasma Proc., 5 (4), 391 (1985).

5. T.W. Petrie and E. Pfender, Warme-und Stoffubertragung, 5 (2), 85 (1972).

6. T.N. Meyer and E. Pfender, Warme-und Stoffubertragung, 6 (1), 25 (1973).

7. C.H. Kruger, The Physics of Fluids, 13 (7), 1737 (1970).

8. A. Gleizes, H. Kafrouni, H. Daug Duc, and C. Maury, J. Phys. D.: Appl. Phys., 15, 1031 (1982).

9. K.C. Hsu and E. Pfender, J. Appl. Phys., 54 (8), 4359 (1983).

10. K.P. Nick, J. Richter, and V. Helbig, J.Q.S.R.T., 32 (1), 1 (1984).

11. Xi Chen and E. Pfender, Plasma Chem. and Plasma Proc., 3, (1), 97 (1983).

12. R. Paulson and E. Pfender, Warme-und Stoffurbertragung, 6(1), 62 (1973).

13. H.A. Dinulescu and E. Pfender, J. Appl. Phys., 51 (6), 3149 (1980).

14. N.A. Sanders and E. Pfender, J. Appl. Phys., 55 (3), 714 (1984).

15. K.C. Hsu and E. Pfender, J. Appl. Phys., 54 (7), 3818 (1983).

10.2 PLASMA-SOLID BOUNDARIES: SHEATH EFFECTS

S. A. SELF
Stanford University
Mechanical Engineering Department
Stanford, California 94305

The interaction between a thermal plasma and an electrode is complex and technically important because of electrode erosion and contamination of the plasma. At low current densities, current transfer at both cathodes and anodes is diffuse, but above a certain current density, higher for anodes than cathodes and dependent on electrode temperature and surface properties, constriction occurs to form localized cathode arc spots and anode glows.

To elucidate the mechanisms of current transfer, a simple, 1-D, continuum model of an isothermal, collision-dominated plasma contacting a plane electrode has been developed which allows for electron or ion emission. The plasma is assumed to be in equilibrium by a balance between electron impact ionization and 3-body recombination on electrons. The governing equations are those of continuity and momentum transfer for electrons and positive ions, together with Poisson's equation for the self-consistent electric field. This nonlinear equation set is solved numerically for the five variables n_e, n_i, Γ_e, Γ_i, and E, from which the potential ϕ is then obtained by quadrature. The boundary conditions are as follows. In the distant plasma ($x \to \infty$), $n_e, n_i \to n_\infty$, $\Gamma_e \to -\mu_e n_\infty E_\infty$, $\Gamma_i \to \mu_i n_\infty E_\infty$, and $E \to E_\infty \equiv -J/en_\infty(\mu_e + \mu_i)$ where J is the current density. At the electrode ($x = 0$), $n_e = n_e(0)$, $n_i = n_i(0)$, prescribable constants which can be related to the saturated emission current densities of electrons and ions.

There are two scale lengths for the problem: the Debye length $\lambda_D \equiv (\epsilon_0 kT/n_\infty e^2)^{1/2}$ and the ion recombination length $\ell_R \equiv (2D_a/\beta n_\infty^2)^{1/2}$, where D_a is the ambipolar diffusion coefficient and $n_\infty\beta(T)$ is the 3-body recombination coefficient. Typically the ratio $\epsilon \equiv (\lambda_D/\ell_R) \ll 1$, which makes the equation set stiff. The variables are non-dimensionalized on the following reference values: x on ℓ_R; n_e, n_i on n_∞; $\dot{n}$, the net volume generation rate on $\dot{n}_R \equiv \beta n_\infty^3$; ϕ on $\phi_R \equiv (kT/e)$; E on $E_R \equiv (\phi_R/\ell_R)$; the fluxes on $\Gamma_R \equiv n_\infty(2D_a/\ell_R)$, and the current densities $J_e \equiv -e\Gamma_e$, $J_i \equiv e\Gamma_i$ on $J_R \equiv [(1 + \mu^2)/4\mu]e\Gamma_R$. Non- dimensional variables are denoted by an overbar. There are five specifiable dimensionless parameters: ϵ, $\mu \equiv (\mu_i/\mu_e) \ll 1$, a weak function of gas type; $\bar{n}_e(0)$ and $\bar{n}_i(0)$; and $\bar{J}$.

The equation set is solved uniformly throughout the region ($0 \le \bar{x} \le \infty$) with no arbitrary division into plasma and sheath regions, with questionable matching conditions, as has often been done hitherto. However, when $\epsilon \ll 1$, the solutions assume the following structure. Adjoining the electrode is a non-neutral sheath of scale λ_D, followed by a quasi-neutral ionization nonequilibrium layer, of scale ℓ_R where there is net generation of electron-ion pairs, which in turn merges smoothly into the uniform plasma. Allowance for imbalance of generation and recombination, and the resulting occurrence of a region of net generation, is essential for the correct treatment of the problem, as emphasized below.

An analytic solution is obtained [1] in the quasi-neutral approximation ($\epsilon \to 0$) by putting $\bar{n}_e = \bar{n}_i = \bar{n}$ and neglecting Poisson's equation. This solution describes the ionization nonequilibrium layer and plasma, but not the sheath.

With the boundary condition $\bar{n}(0) = 0$, we have:

$$\bar{n} = \tanh \bar{x} \tag{1}$$

$$\dot{\bar{n}} = \operatorname{sech}^2 \bar{x} \tanh \bar{x} \tag{2}$$

$$\bar{E} = [-(1 - \mu)/(1 + \mu) \operatorname{sech}^2 \bar{x} + \bar{J}] \coth \bar{x} \tag{3}$$

$$\bar{\Gamma}_e = -(1/2) [\operatorname{sech}^2 \bar{x} + \bar{J}(1 + \mu)/2\mu] \tag{4}$$

$$\bar{\Gamma}_i = -(1/2)[\operatorname{sech}^2 \bar{x} - \bar{J}(1 + \mu)/2] \tag{5}$$

In (1) and (2) $\bar{n}$ and $\dot{\bar{n}}$ are independent of μ and $\bar{J}$, while $\dot{\bar{n}}$ has a maximum of ~0.385 at $\bar{x}$ ~0.658 such that the total generation rate $\int \dot{\bar{n}}\, d\bar{x} = (1/2)$. In (3), $\bar{E}$ has two components; an ambipolar term directed towards the electrode, and a resistive term proportional to $\bar{J}$. Both terms have a pole at $\bar{x} = 0$, so that $\bar{\phi}$ has a logarithmic singularity. To obtain a finite potential difference between the plasma and electrode requires solution of the full equations so that the sheath is included. The fluxes in (4) and (5) also have an ambipolar component directed towards the electrode plus a second term associated with the current. For zero current, there are equal fluxes, $\bar{\Gamma}_e(0) = \bar{\Gamma}_i(0) = -(1/2)$ to the electrode, which collects all the electron-ion pairs generated in the ionization nonequilibrium layer, represented by $\int \dot{\bar{n}}\, d\bar{x} = 1/2$.

Certain important and novel results can be obtained from this quasi-neutral solution concerning the existence of three distinct critical current densities.

For a cathode ($\bar{J} < 0$), as $(-\bar{J})$ is increased, the collected electron flux decreases rapidly and the collected ion flux increases slowly, while the electric field and potential drop become more negative. When $-\bar{J}$ reaches the critical value $\bar{J}_c \equiv 2\mu/(1 + \mu) \ll 1$, $\bar{\Gamma}_e(0) \to 0$ and it is clear that $(-\bar{J})$ cannot exceed this value for a non-emitting cathode. This limiting cathode current is quite small, much less than the value $(en_\infty \bar{c}_i/4)$ often taken as the ion current density that can be drawn from a plasma into a cathode sheath. Physically, the reason for the limiting cathode current is that at the limit, all the electrons generated in the ionization nonequilibrium layer migrate into the plasma, constituting almost all of the total plasma current $\bar{J} = \bar{J}_e + \bar{J}_i$. Since the total net generation is limited ($\int \dot{\bar{n}}\, d\bar{x} = 1/2$) no greater electron current can flow in the absence of cathode emission because the ionization nonequilibrium layer is the only source of electrons. Under limiting conditions, at the cathode the total current is carried by the flux of arriving ions $\bar{\Gamma}_i = -(1/2)(1 + \mu)$, of which $-(1/2)$ is generated in the ionization nonequilibrium layer and $-(1/2)\mu$ is drawn from the plasma.

For an anode ($\bar{J} > 0$) there are two critical current densities. As $\bar{J}$ increases from zero, the electron flux to the anode increases rapidly and the ion flux decreases slowly, while the electric field and potential drop become less negative. When $\bar{J} = \bar{J}_{A1} \equiv (1 - \mu)/(1 + \mu)$, $\bar{E} \to 0$, and for larger currents $\bar{E}$ and the potential drop become positive. This corresponds to a transition from a negative potential fall to a positive one, a phenomenon well known to occur with

increasing anode current but hitherto not, apparently given a simple quantitative explanation. At potential inversion, $\bar{J} = \bar{J}_{A1}$, the electron flux to the anode has increased greatly to $\bar{\Gamma}_e(0) = (-1/2)[1 + (1 - \mu)/2\mu] \sim -(1/4\mu)$ while the ion flux has decreased to $\bar{\Gamma}_i(0) = (-1/2)[1 - (1-\mu)/2] \sim -(1/4)$.

As the anode current density is increased above $\bar{J}_{A1}$, the positive potential fall increases, the collected electron flux increases further, while the collected ion flux decreases until for $\bar{J} = \bar{J}_{A2} \equiv 2/(1 + \mu) \sim 2J_{A1}$, $\bar{\Gamma}_i(0) \to 0$ and the current density to an anode cannot exceed this value in the absence of ion emission. Physically the reason for the limiting anode current density $\bar{J}_{A2}$ is that at this limit all the ions generated in the ionization nonequilibrium layer migrate into the plasma and constitute the uniform ion current there. Of course, the electron flux (from infinity) is much larger than the ion flux in the uniform plasma, but they are constrained to satisfy $\bar{\Gamma}_{i\infty} = -\mu\bar{\Gamma}_{e\infty}$, so that the limited supply of ions near the electrode imposes a limit on the electron current, and, hence, on the total current $\bar{J} = e(\bar{\Gamma}_{i\infty} - \bar{\Gamma}_{e\infty})$.

Numerical solutions of the full set of equations for specified values of $\epsilon \equiv (\lambda_D/\ell_R) \ll 1$ confirm these results from the quasi-neutral approximation. For zero emission ($\bar{n}_e(0) = \bar{n}_i(0) = 0$) and $\bar{J} = 0$, a smooth transition from the ionization nonequilibrium layer through a thin positive ion sheath to the electrode is obtained. The potential fall from plasma to electrode, given by $\Delta\bar{\phi} = -[6 + (2/3)\ \ell n(1/\epsilon)]$, increases logarithmically with decreasing ϵ. By arbitrarily defining the plasma-sheath "boundary" as occurring where $2(n_i - n_e)/(n_i + n_e) = 0.1$, an estimate of the ion-sheath thickness is obtained as

$$\Delta x_s \simeq 3.7\epsilon^{-1/3}\lambda_D, \tag{6}$$

which is many Debye lengths thick. The total generation rate $\int \bar{n}\, d\bar{x}$ is insensitive to ϵ and tends to the quasi-neutral solution value (-1/2) as $\epsilon \to 0$.

For zero emission, numerical solutions as a function of current density confirm the conclusions from the quasi-neutral approximation when $\epsilon \ll 1$. For a cathode, as the current is increased, the ion-sheath thickness and the potential fall increase. As $(-\bar{J}) \to \bar{J}_c$ the electron flux to the cathode tends to zero and the potential fall increases indefinitely, corresponding to current saturation. [For $\bar{J} \neq 0$, the potential fall is defined as the difference between the actual electrode potential and that found by extrapolation of the linear potential variation in the distant plasma.] For an anode at $\bar{J} \simeq \bar{J}_{A1}$, the potential fall inverts from negative to positive. For higher currents the positive ion sheath is replaced by an electron-rich sheath which increases in thickness with increasing $\bar{J}$. As $\bar{J} \to \bar{J}_{A2}$, the ion flux to the anode tends to zero and the positive potential fall increases indefinitely corresponding to current saturation.

The fact that the limiting currents given by the quasi-neutral approximation are confined by the full numerical solutions is due to the fact that they are associated with the finite net generation rate in the ionization nonequilibrium layer. Because, for this layer, quasi-neutrality applies, then for $\epsilon \ll 1$, the net generation rate $\bar{n} = \int \bar{n}_e(1 - \bar{n}_e\bar{n}_i)d\bar{x}$ is quite insensitive to the value of ϵ and tends to the quasi-neutral value of (1/2) as $\epsilon \to 0$.

The effect of electron emission on the cathode boundary layer is found by imposing a nonzero value of the electron concentration $\bar{n}_e(0)$ as an electrode boundary condition, while retaining $\bar{n}_i(0) = 0$. These conditions imply that there

is an electron-rich sheath adjoining the electrode. For $(-\bar{J}) < \bar{J}_c$, a thin electron sheath is interposed between the cathode and the positive ion sheath. This electron sheath reduces the electric field strength near the cathode and, with it, the potential fall for a given current. As $\bar{n}_e(0)$ is increased, the electron sheath increases in strength and thickness, and the potential fall decreases until, for a certain value $\bar{n}_e(0)_{crit}$, the electric field at the cathode $\bar{E}(0) \to 0$. The condition $\bar{E}(0) = 0$ is identified with the onset condition for space-charge limited electron emission in consonance with the terminology for thermionically emitting vacuum diodes. For further increase of $\bar{n}_e(0)$, $\bar{E}(0)$ changes sign to positive (a decelerating field for emitted electrons) and a weak potential minimum (a virtual cathode) forms just in front of the cathode, while the potential fall continues to decrease, but very slowly when the cathode is (electron) space-charge limited.

The value of $n_e(0)$ can be related to the emitted electron current density, which is given by the Richardson-Dushman law

$$J_e^+(0) = (-e/2)[n_e(0)(\bar{c}_e/2) + \Gamma_e(0)] = -AT^2 \exp(-\phi_w/kT) \tag{7}$$

where ϕ_w is the work function and $A \simeq 1.2 \times 10^6$ A/m^2 K. The value of $n_e(0)$ (and hence of saturated emission capability $J_e^+(0)$) necessary to produce space-charge limited conditions is an increasing function of $(-\bar{J})$.

The presence of electron emission removes the current limitation phenomenon at $(-\bar{J}) = \bar{J}_c$ and, depending on the emission capability, allows much larger currents to flow. By cross-plotting the computed results, a graph of the cathode potential fall versus current density can be obtained, with the saturated emission current $J_e^+(0)$ as parameter. These voltage-current characteristics have the following general trends. For $J_e^+(0) \neq 0$, and small currents, $\Delta\bar{\phi}$ is smaller (for a given value of $(-\bar{J})$) and increases slowly with increasing $(-\bar{J})$ while the cathode remains electron space-charge limited, i.e., while there is a potential minimum in front of the cathode. When $(-\bar{J})$ reaches a value $\sim J_e^+(0)$ the potential minimum disappears, $\bar{E}(0)$ changes sign from positive to negative and the cathode becomes emission-limited. For further increase of current $\Delta\bar{\phi}$ increases much more rapidly with $(-\bar{J})$ (than in the space-charge limited regime).

A parallel study has also been made of the effect of ion emission on the anode boundary layer. When $\bar{J} > \bar{J}_{A1}$ and there is an electron sheath and a positive anode fall, the emission of ions produces a thin ion sheath adjoining the anode and reduces both the field near the anode and the potential fall. Anode ion emission also removes the current limitation at $\bar{J} = \bar{J}_{A2}$. However, the occurrence of ion emission from an electrode is limited to the situation when the surface work function is less than the ionization potential of a plasma specie. Thus while ion emission is relevant to thermionic converters, it is not generally present in most thermal plasma-electrode systems.

While the results outlined above are derived from an admittedly simple model, they do lead to a general understanding of the nature of the plasma-electrode boundary layer and constitute a first step to more detailed analysis. In particular the model shows the existence of the critical current densities $\bar{J}_c$, $\bar{J}_{A1}$, and $\bar{J}_{A2}$ and how they are related to the finite net generation rate of electron-ion pairs in the ionization nonequilibrium layer. It also illuminates the structure of the sheath when there is electron emission at a cathode and how the potential fall-current density relation depends on the electron emission capability.

The principal limitation of the model is that the plasma is assumed to be isothermal. Currently, the model is being generalized to include an electron energy equation with T_e as an additional variable. This allows the electron temperature to be elevated above the heavy species temperature as a result of Joule heating where J•E is positive. This term is large in the cathode sheath when the cathode is emission limited and in the anode sheath when $\bar{J} > \bar{J}_{A1}$ and there is a positive anode fall. The electron temperature elevation produces a significant increase in the net generation rate which allows a larger current to flow for a given potential fall.

A second limitation is that the model is one-dimensional. To account for the transition from a diffuse mode of current transfer to a constricted one, a linear perturbation analysis should be performed on the one-dimensional system, allowing for perturbations in the transverse direction. Such an analysis should yield the conditions for the onset of localized cathode arc spots and of anode glows as a result of construction due to electrothermal instability.

References

[1] S. A. Self and L. D. Eskin, "The Boundary Layer Between Electrodes and a Thermal Plasma," IEEE Trans. Plasma Science, PS-11, 274-285 (Dec. 1983).

10.3 DISCHARGE INSTABILITIES IN SEEDED COMBUSTION PLASMAS (MHD GENERATORS)

ROLF HERNBERG
Tampere University of Technology
Tampere, Finland

Problem Characterization

The study pertains to alkali seeded combustion plasmas at or above atmospheric pressure, typical of open cycle MHD generators. The plasma temperature is 3000 K to 2500 K. The electron concentration is about 10^{18} to 10^{20} m^{-3} in the flow core, but may be substantially lower in the boundary layers. The plasma core is close to LTE. In the boundary layers strong non-equilibrium effects may occur:

- charge separation, leading to sheath formation near the electrodes. In some cases sheath thicknesses can be substantially greater than the Debye length.
- ionization nonequilibrium
- temperature separation ($T_e > T$)

The objective has been to study the mechanisms limiting the diffuse discharge of electric current to the electrodes and leading to discharge constrictions.

Phenomenology

In a typical large-scale open cycle MHD generator the average current density is about 1 A/cm^2. The surface area of one electrode segment could be typically about 100 cm^2. Thus the total current per electrode segment is of the order 100 A. This current may be transferred to the electrode from the plasma core through the boundary layer in different ways:

* by diffuse discharge (desirable)
* by a variety of constricted discharges:
* micro-arcs; ~ 0.1 to 20 A per micro-arc, i.e. ~ 5 to 1000 simultaneous micro-arcs per electrode segment (acceptable, the larger the number, the better),
* high-current arcs of the order 100 A, (prohibitive)
* temporary, spark-like constrictions

In order to control and improve the uniformity of current transfer one needs to know the physical mechanisms underlying the instabilities, which lead to constriction of the current. The type of discharge instabilities and operating conditions at the anode and cathode in seeded combustion plasmas is summarized in Table I.

Table I. Discharge Instabilities on MHD Generator Electrodes

POLARITY	ANODE		CATHODE	
surface condition	"cold" (seed deposition)	"hot	non-emitting	emitting
surface temperature	300...1000 K	≥ 2300 K	< 1500 K	> 1500 K
instability type	electrothermal in seed layer	electrothermal in electrode material $^{\alpha}$ or plasma b. layer$^{\beta}$	electrostatic in sheath	electrostatic or electrothermal in el.mat$^{\alpha}$. or plasma b.layer$^{\beta}$
critical current density	0.5...1 A/cm^2	up to 10 A/cm^2 and more	10^{-2}...10^{-1} A/cm^2 (at local heat fluxes in excess of 5 MW/m^2: > 1 A/cm^2)	< 1 A/cm^2
surface phenomena important?	yes	yes$^{\alpha}$ no$^{\beta}$	yes	yes$^{\alpha}$ no$^{\beta}$
important surface parameter	transport properties of seed material deposited on surface	transport properties of electrode material (ceramic)	secondary emission coefficient	work function; transport properties of electrode mat.

Observations

Some observations of potentially general interest are the following.

* Thermal and electrical effects are strongly intertwined. When electrical performance is fixed by operational requirements, the discharge can be affected by thermal means (electrode temperature and local thermal flux) and through surface conditions (material properties).

* With increasing current density a diffuse discharge will ultimately become electrothermally unstable in the plasma boundary layer, unless there is another instability mechanism which becomes activated at a lower current density, like

- electrothermal instability in the solid electrode material or in a layer deposited on the surface.

- electrostatic "breakdown" of the sheath on cathodes.

* In a quasi-neutral plasma, the current continuity requirement is a very effective mechanism for current limitation, since, for quasi-neutrality to apply in absence of diffusion:

$$j_e/j_i = \mu_e/\mu_i \; ; \quad \text{hence} \quad j_e \gg j_i \quad .$$

References

1. R. Hernberg, T. Karema, K. Nousiainen, J. Vattulainen, V.V. Kirillov, A.I. Romanov, M.A. Sheindlin, A.S. Tikhotsky: Current Transfer to Hot Ceramic Electrodes in a Molecular Plasma Flow. 9th Int'l. Conf. MHD El. Power Generation, Tsukuba, Japan, November 17 - 21, 1986.

2. R. Hernberg, K. Nousiainen, A.S. Tikhotsky: Stability of Diffuse Current Transfer to "Cold" Electrodes in Open-Cycle MHD Generators. Ibid.

Luncheon group. CCW from 7:00: J. Elliot, T. Yoshida, H. Casey, J. Feinman, D. Mac Rae, D. Harris, G. Vogt, and H. Anderson

Luncheon group. Left to right: C. Holden, S. Self, R. Hernberg, J. Kunc, P. Fauchais, A. Larson, and C. Cremers.

CHAPTER 11

PLASMA-SURFACE CHEMISTRY AND HEAT TRANSFER

Session Chairman

M. Venugopalan
Department of Chemistry
Western Illinois University
Macomb, Illinois 61455

11.1 CHEMICAL REACTIVITY AND CATALYTIC EFFECTS IN HETEROGENEOUS PLASMA ENVIRONMENTS

M. VENUGOPALAN
Department of Chemistry
Western Illinois University
Macomb, Illinois 61455

In thermal plasma systems "cold" materials at high pressures flow into "hot" plasma regions of varying temperatures (3000-30,000K) and are subsequently quenched at very fast rates (10^5-10^8 Ks^{-1}) to yield the desired products. Although heat transfer from plasmas depends on a multitude of processes, sometimes high energy efficiencies may be achieved. However, it is rarely possible to isolate the intermediates in a collision-dominated system and postulate reaction mechanisms.

Chemical yields in homogeneous reactions are often commensurate with what one would expect from thermodynamic equilibrium compositions at the reaction temperatures. For heterogeneous reactions they are often lower or higher than expected. Heterogeneity is typically inherent in the system because of electrode (arcs) and/or wall (high frequency) processes. It may be introduced by way of reactants (solid + gas, as in the case of C(s) + H_2) or produced by way of products (decomposition of acetylene, synthesis of carbides and nitrides from chlorides). Surely, the vaporization/condensation barriers may be expected to produce lower/higher chemical yields. It has been pointed out that catalytic processes are the only realistic way of increasing the chemical yield.

The (arc) electrodes can function as a catalyst for reactions occurring with low yield in the bulk plasma. For example, the combustion of hydrogen in an atmospheric pressure plasma to form water is accelerated considerably by using aluminum electrodes. However, the formation of temperature-sensitive molecules such as O_3, H_2O_2, NH_3, NO and so forth is retarded. The extreme values of temperature, current density and field strength prevailing in the regions close to the electrodes, in particular the heat condensation at the anode, and the gradients of these parameters make heat transfer studies difficult, if not impossible. The work of Eckert and Pfender [1, 2] on this subject is extensive, but diagnostics of this region remains a 'formidable task'.

On the other hand, the electrodes can supply contaminants to the bulk plasma, which influence the activation/deactivation of the excited states of the various plasma constituents. Amouroux et al. [3] have examined modifications of plasma reactivity by vibrational excitation. More detailed work is needed to delineate catalytic processes in the plasma gas from those on the solid surface.

For viscous flow, plasma velocity must be zero at the wall. Under given flow-conditions, for example, large Re numbers, velocity cancellation occurs in a thin layer, the so-called boundary layer, close to the rigid wall surface. Generally, the wall acts catalytically and increases largely the reaction. Therefore, the species' concentrations are not the same on the two frontiers of the boundary layer and diffusion of these species will occur, mass transfer thus being superimposed to heat transfer through the boundary layer. Lassau [4] investigated this transfer mechanism using a nitrogen plasma flow and found catalysis to occur on a flat steel plate, but not a Pyrex plate parallel to the stream. Pfender [5] has proposed that recombinations result in a low density of charged species in the boundary layer which then acts as a thermal insulator and prevents a large

increase in heat transfer. Although catalytic processes in some combustion reactions (hydrogen, methane) have been investigated, this is a field which requires considerable research and application in the future.

Surface treatment of materials is dependent upon the characteristics of the boundary layer. However, most of this type of work has been done using low pressure-low temperature glow discharge. To a large extent, work in the area of thermal plasma (coatings, for example) has developed by empirical means with relatively little scientific understanding.

When heterogeneity is introduced by way of reactants or produced by way of products, vaporization and condensation phenomena play crucial roles in making useful products. Acetylene production from coal and synthesis of metal compounds or ceramics are examples. Models for the plasma-particle heat transfer assume that the particles have a uniform temperature or include the internal heat conduction in the particles. Measurements by Bourdin, Fauchais and Boulos [6] show that temperature differences as high as 1000K could develop between the surface and the core of alumina particles 20 μm in diameter when immersed in a nitrogen plasma at 10,000K. Experiments are needed to delineate the conditions for including/excluding the effects of internal heat conduction in particles under chemical reaction conditions.

Heterogeneous environments form the basis of some plasma decomposition reactions. The recent experiments of Amouroux, et al. [3] in which an argon plasma (5000K) was injected into a fluidized bed of limestone powder demonstrated that the decomposition process ($CaCO_3 \rightarrow CaO + CO_2$) is diffusion-controlled. A chemical reaction model [7] which involves heat transfer from the plasma to the boundary layer, actually a reactive interface, and transport of the gaseous products through this interface to a region where the chemical reactions are controlled by the slowest of the processes appears to be satisfactory.

Finally, enhancement of plasma-chemical conversion and product selectivity have been reported due to the presence of a foreign substance, such as a transition metal or its oxide, in the plasma, in the flowing afterglow or both [8]. However, most similar investigations have been made using low-temperature (350-700K) low- and intermediate-pressure (0.1-100 torr) plasmas [9]. Thermal plasmas at high temperatures (3000-15,000K) do not lend themselves for these investigations because few solids exist and/or exhibit catalytic activity at these temperatures at 1 atm pressure. We are, therefore, investigating the range of intermediate temperatures (800-1600K) using magnetically rotating arcs of coaxial design operating at 5-10A [10]. The flowing afterglows from these arcs appear to be ideal for catalytic investigations with mass throughput at normal pressure. Optimization is needed for such experimetnal variables as arc current, mass flow rate, and the locations of the reactant injection, catalyst and quenching. Research in this area may serve as the lead for other applications of chemical plasma synthesis.

References

1. E.R.G. Eckert and E. Pfender, "Advances in Plasma Heat Transfer," in Advances in Heat Transfer (J.P. Hartnett and T.F.Irvine, Jr., eds.), Academic Press, New York, Vol. 4, p. 270 (1967).

2. E. Pfender, Pure & Appl. Chem., 48, 199 (1976).

3. J. Amouroux, A. Gicquel, S. Cavvadias, D. Morvan and E. Arefi, Pure & Appl. Chem., 57, 1207 (1985).

4. G. Lassau, Chem. Ind., Genie Chim. 100 (7), 1074 (1968); C.R. Acad. Sci., 261, 4617 (1965).

5. E. Pfender, "Electric Arcs and Arc Gas Heaters," in Gaseous Electronics (M.N. Hirsh and H.J. Oskam, eds.), Academic Press, New York, Vol. 1, p. 291 (1978).

6. E. Bourdin, P. Fauchais and M.I. Boulos, Int. J. Heat Mass Transfer, 26, 567 (1983).

7. C. Bonet, Réunion R. C. P. Gaz Ionisés Réactifs, Paris, (P. Fauchais, ed.), Limoges University, October (1978).

8. E. N. Eremin, Russ. J. Phys. Chem., 49, 1112 (1975).

9. M. Venugopalan and S. Veprek, "Kinetics and Catalysis in Plasma Chemistry," in Plasma Chemistry IV (Topics in Current Chemistry No. 107), Springer Verlag, Berlin-Heidelberg-New York, 1983, pp. 1-58.

10. A. J. Jacobson, V. Vukanovic and M. Venugopalan, Proc. Seventh Int. Symp. Plasma Chem., Vol. 2, p. 378, Eindhoven, (1985).

11.2 HEAT TRANSFER AND CHEMICAL REACTIONS IN HETEROGENOUS ENVIRONMENTS

P. FAUCHAIS
Laboratorie Thermodynamique
Université de Limoges
87060 Limoges Cedex, France

Heat transfer and chemical reactions between condensed particles and thermal plasmas depend on the particle trajectories and the resulting thermal histories or more precisely the conditions to which the particles will be exposed. Of course, heat and momentum transfer are much more complex with thermal plasmas than with ordinary gases due to the presence of charged particles, chemical reactions, nonlinear thermal and transport properties and steep gradients.

Once the velocity and temperature distributions of the plasma are known and supposed, at first approximation, nonperturbed by the particles or the injection carrier gas, the trajectory of one particle can be calculated. As recalled by Pfender [1] it depends on:

• the modified viscous drag, due to strongly varying plasma properties: in most cases semiempirical relationships for $Re < 100$ are used for the drag coefficient when considering particles whose diameter is smaller than 100 μm and these values are corrected either by two factors (one proposed by Lewis and Gauvin [2] and the other by Lee, Hsu and Pfender [3]) or by calculating a mean integrated value of the plasma transport properties between particle surface temperature and plasma far away from it. However at the moment [1] the best method is not clearly defined.

• noncontinuum effects when the mean free path of the gas is no longer smaller (1/100) than the particle diameter (this occurs at atmospheric pressure for particles smaller than 20 μm and for bigger particles as soon as pressure decreases). A correction term has been proposed by Chen and Pfender [4], however the validity of the equation has not been proven (lack of a basis of comparison) and the value of the accommodation coefficient is to be guessed.

• thermophoresis that can play a role for temperature gradients higher than 10^7 K/m and small particles. However, as underlined by Pfender [1] thermophoresis is relatively unimportant in the penetration stage of the particle because of the high relative velocities and its importance is also questionable in the second stage since temperature gradients decrease rapidly in regions remote from the fringes of the jets and residence times are very short (about 1 ms).

• turbulence: when the plasma velocity field is locally modified by randomly oriented turbulent eddies, dispersed trajectories of single particles can be obtained for diameter smaller than 10 μm [5].

• particle evaporation specially for ceramics with low thermal conductivity when immersed in a high thermal conductivity plasma (those containing hydrogen, for example). The vapor cloud modifies the plasma transport properties but unfortunately these modifications cannot be calculated at the moment; however, the mass losses can be taken into account for the trajectories calculations.

• particle shape (most of the calculations have been performed for spherical particles) as well as particle charging may also affect the trajectories but unfortunately these effects have not been studied yet.

• Bassett history term at least is generally much less than the viscous drag for particle sizes $< 100\ \mu m$ and thus can be neglected.

Once the trajectory of one particle is known, the heat transfer can be calculated. It depends [1] on:

• the heat transfer inside the particles that plays a role as soon as the ratio of the mean integrated thermal conductivity of the plasma between the surface temperature and that of the plasma far from the particle is higher than 0.03 times the thermal conductivity of the particle [6]. It means, for example, that with ceramic particles the surface can reach the boiling temperature while the center of the particle is still far below the melting temperature.

• the Nusselt coefficient (including conductive and convective terms) with either correction factors to take into account the strongly varying properties of the plasma or using the mean integrated thermal conductivity to determine the heat transfer coefficient from it, the "good" choice between these different conditions being still unknown [1].

• the vaporization or evaporation of the particle modifying the transport properties close to the particle.

• the noncontinuum effects reducing the heat transfer to the particle.

As soon as trajectories and surface temperatures of single particles with given masses and injection velocities have been calculated and if the distributions of particle sizes and injection velocities are known, the corresponding distribution of trajectories and temperature histories can be calculated for a given plasma flow [7,8]. It is worthwhile to underline that the resulting trajectories distribution depends on the product of particle size and injection velocity distributions and that this product is great for small particles with narrow size distribution (but with a large injection velocity distribution) or for bigger particles with large size distribution (narrow injection velocity distribution).

Of course, all these calculations assume that the plasma flow is not perturbed by the particle carrier gas, that the cylindrical symmetry is conserved and that the plasma is not cooled by the particles injection. Perturbation of the plasma by the cold carrier gas is certainly to be developed (3D flow model) specially for small particles which necessitate a high momentum of the carrier gas perturbing the plasma flow as shown by the measurements of Gravelle and Boulos [9] or of Coudert and Fauchais [10]. Charge effect (cooling of the plasma) can be calculated through an iterative procedure, as shown by Boulos [11], the flow being calculated first with no particles and then the cooling by the particles present in one element of the grid being introduced as a source term. This cooling effect becomes very sensitive with the evaporation of small particles and, in general, has to be taken into account for spraying plasma jets or RF atmospheric plasma generation as soon as the particle flow rate is higher than 1 kg/h.

With such complex two phase flows (even with no chemical reactions) it is necessary to perform measurements on the plasma flow and on the particles to verify if the used assumptions are realistic and to determine the Nusselt and Drag coefficients. This, which implies to measure simultaneously the plasma velocity and temperature fields, the particle trajectory, velocity and surface temperature distribution has been started since a few years at the University of Limoges.

However it proceeds very slowly because the techniques are very difficult:

• plasma temperature (heavy species temperature) is now well established, the measurements being performed through rotational spectra with an OMA 2D as detector [10,12].

• plasma velocity measured by introducing small particles ($< 3\ \mu m$) in the plasma arc chamber [13] or by axial injection in RF plasmas [14] does not present a high precision and Doppler effect from atomic lines is usable only for spraying plasma jets below about 50 Torr.

• particle-velocity distribution (diameter higher than $3.5\ \mu m$) can be reached with a good precision in small measurement volumes (smaller than a sphere of 0.5 mm in diameter) either by laser Doppler anemometry or the two point focus method and the measurements can be performed even in the plasma core [15].

• distribution of surface temperature of the particles can be measured by two-color pyrometry outside the plasma core [16] but the measurement volume is not very small (ϕ=150 μm, ℓ=10 mm) - inside the plasma core the surface temperature may be reached indirectly through the evaporation of the particles measured by absorption technique.

Because of all these difficulties, it is only now that the first measurements of C_D and Nu in the plume of a spraying plasma jet will be published (University of Limoges).

Finally, chemical reactions must be considered. Two models have been developed [17]:

• continuous reaction model where the concentration of the condensed reagent is constant across the condensed phase (no mass transfer resistance of the gaseous products across the condensed phase). This model seems rather suitable for decomposition reaction or for evaporation and is controlled either by diffusion or heat transfer, but measurements are still lacking.

• shrinking core model, which invokes the following steps: heat transfer of the plasma towards the reactive interface, transport of gaseous products through the reactive interface to the outside where the chemical reactions are controlled by the slowest of the different processes. A few measurements have been performed in plasma fluidized beds where the residence times are long enough for complete reactions to proceed. For example Arnould and Amouroux [18] studying the decomposition of calcite have shown that this process is essentially controlled by external diffusion.

References

1. E. Pfender, Pure and Applied Chemistry, 57 (9), 1179 (1985).

2. J.A. Lewis, W.H. Gauvin, AIChE J., 19, 982, (1973).

3. Y.C. Lee, K. Hsu, E. Pfender, Proc. 5th Int. Symp. on Plasma Chem., 2, 785 (ed) Prof. Waldie, Univ. of Edinburgh, (1981).

4. X. Chen, E. Pfender, Plasma Chem. Plasma Proc., 3, 97 (1983).

5. Y. Lee, E. Pfender, Plasma Chem. Plasma Proc., 5, 3 (1985).

6. E. Bourdin, P. Fauchais, M.I. Boulos, Int. J. Heat and Mass Transfer, 26, 567 (1983).

7. P. Proulx, J. Mostaghimi, M.I. Boulos, Int. J. Heat and Mass Transfer (1985).

8. A. Vardelle, M. Vardelle, B. Pateyron, P. Fauchais, Proc. 7th Int. Symp. on Plasma Chemistry, 2, 898, (ed.) Prof. Timmermanns, Univ. of Eindhoven, N.L. (1985).

9. D. Gravelle, M. Baulieu, C. Carlone, M. Boulos, Proc. 6th Int. Symp. on Plasma Chemistry, 1, 108, (ed.) Prof. Boulos, Univ. of Scherbrooke, C.N. (1983).

10. J.F. Coudert, P. Fauchais, Proc. 7th Int. Symp. on Plasma Chemistry, 7, 760 (ed.) Prof. Timmermanns, Univ. of Eindhoven, N.L. (1985).

11. M.I. Boulos, Pure and Applied Chem., 57 (9), 1321 (1985).

12. J.F. Coudert, J.M. Baronnet, P. Fauchais, Proc. 6th Int. Symp. on Plasma Chemistry, 1, 102, (ed.) Prof. Timmermanns, Univ. of Eindhoven, N.L. (1985).

13. A. Vardelle, M. Vardelle, P. Fauchais, Plasma Chem. Plasma Proc. 2, 255 (1982).

14. J. Lesinski, R. Gagné, M.I. Boulos, Proc. 5th Int. Symp. on Plasma Chem., 2, 527, (ed.) Prof. Waldie, Univ. of Edinburgh (1981).

15. M. Vardelle, A. Vardelle, P. Fauchais, M. Boulos, AIChE J., 29 (2), 236 (1983).

16. J. Mishin, M. Vardelle, J. Lesinski, P. Fauchais, J. of Physics : E (to be published).

17. C. Bonet, Chem. Eng. Progr., 72, 12 (1976).

18. P. Arnould, S. Cavadias, J. Amouroux, Proc. 7th Int. Symp. on Plasma Chemistry, 1, 195, (ed.) Prof. Timmermanns, Univ. of Eindhoven, N.L. (1985).

THERMAL PLASMA RESEARCH AREAS

CHAPTER 12

PLASMA-PARTICULATE INTERACTIONS

Session Chairman

E. Pfender
Mechanical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

12.1 PLASMA PARTICULATE INTERACTIONS: MOMENTUM AND HEAT TRANSFER

P. FAUCHAIS
Laboratorie Thermodynamique
Universite de Limoges
87060 Limoges Cedex, France

Modeling

Let us, for example, consider a DC a plasma jet used for spraying. One can determine the momentum and heat transfer to a single particle in two ways: one is modeling, one is measurement. For modeling, let us consider first a single particle. The trajectory of the particles depends strongly on the viscous drag coefficient which has to be corrected to account for the very high temperature gradients that exist in the plasma, especially in the boundary layer close to the particle [1-5]. The first problem that arises is what gas you consider to calculate the viscosity and transport properties of the plasma gas around the particle: is it a pure gas, that is to say, a gas which has not been modified by the evaporation of the particle or the entrainment of the gas surrounding the plasma jet. A second aspect of the problem is which temperature do you use. Is it the temperature far from the particle, is it the film temperature, or what? How do you correct for the steep variation of the properties? Is it the mean or integrated value? The question is open.

Once you have solved this problem, a second problem arises for the heat transfer. You know the trajectory of the particles, you know the plasma temperature along this trajectory, so you can calculate the conductive and convective heat transfer to the particle, the radiative exchange, but also you have to take into account the vaporization of the particles, especially for the heat propagation phenomenon [4]. The heat propagation phenomenon occurs as soon as the ratio of the mean thermal conductivity of the plasma to the thermal conductivity of the particles is about 0.03 or higher. This is, for example, the case when you have a ceramic particle in plasma containing hydrogen. And in that case, you may have a very fast evaporation at the surface while the center part of the particle is still cold. This fast evaporation has to be measured and has to be taken into account for the modification of the properties of the plasma jet [6,7]. Moreover, when you use particles, the heat transfer to the particles strongly depends on the morphology of the particle, i.e., on the way it has been manufactured. For example, fused particles, especially for ceramic particles, are rather homogeneous. It is the same when you start with agglomerated particles, which have been sintered afterwards. It's quite different when you consider particles which are simply agglomerated and densified, because now the heat propagation phenomenon is enhanced and you may end up with particles whose surface is well melted but whose central part is not heated at all because the melted surface of the particles makes them sort of balloon out, (blown up by the gas contained by the particles) which limits contact between this melted balloon and the central part of the particle.

A lot of questions arise with respect to the Knudsen effect,i.e., when you consider the value of the mean free path in the gas compared to the diameter of the particle [1]. At atmospheric pressure, for particles smaller than 10 microns, this effect may be important, and is very important as soon as you use a low-pressure plasma, for example, low-pressure plasma spraying at 50 torr. The heat transfer, as well as the momentum transfer, can be reduced by almost one order-of-magnitude by this noncontinuum effect. It means that, for example, at low

pressure, the particles will never follow the plasma velocity and will reach velocities quite comparable to that obtained at atmospheric pressure even if the velocity of the gas is much higher. Under these conditions, it will be very difficult for low-pressure plasmas to melt ceramic particles.

Summarizing this modeling problem, the main questions that arise are (1) the Nusselt numbers and drag coefficients that you have to use, (2) their corrections to account for the steep variations of the plasma properties around the particles, (3) the variation of the transport and thermodynamic properties of the plasma around the particle due to its evaporation, especially for ceramic particles, (4) the modification of plasma composition and its cooling by the entrainment of the gas surrounding the jet, and (5) the heat propagation phenomenon, which also depends on the morphology of the particles.

Particle Distributions, Velocities and Trajectories

If you have calculated the heat transfer to a single particle, you now have to account for the particle size distribution, because usually you have particles with a size distribution, and to overcome the plasma viscosity, these particles must be injected with the proper momentum. This means that they must be injected with an injection velocity that is proportional to their mass. The particles are injected with a carrier gas, which will give a certain velocity profile inside the injector. Finally, you find that the particle trajectory distribution inside the injector will be the result of the product of the size distribution of the particle, as well as the injection velocity profile of the particles [8]. This may result in a very broad trajectory distribution inside the plasma jet. For example, when you use particles with rather small sizes (~ 20 microns) you must have a very broad injection velocity distribution inside your injector, to have a good melting of this particle because, the flow rate of the gas must be high to achieve a high velocity and then the trajectory distribution for these small particles (even if they have a very narrow size distribution) is about the same as the one you obtained for particles of much larger size (~ 40-100 microns). In the latter case, the injection velocity distribution is narrow and you have almost the same trajectory distribution. Thus, one has to keep in mind that all the measurements that could be performed will be stochastic measurements giving results with distributions of trajectory, distribution of velocity, distribution of temperatures, and as I will premise, it is almost impossible to measure a single particle's velocity or surface temperature in flight. The particle loading effect (cooling of the plasma jet by the particles becomes important when the powder loading rate exceeds half of the plasma flowrate [9,10] and cannot be neglected.

Measurements

What can be measured? The plasma temperature can usually be measured with a good approximation. For example, using rotational spectra or excitation temperature when the electron density is higher than 10^{17} cm^{-3}, the temperature is well known [11-17]. However the fast diffusion of the surrounding gas, especially air, has to be taken into account when obtaining the temperature from the population of the excited upper level. The velocity of the plasma is not well known because the Doppler spectral line broadening effect cannot be used [11,18,19] especially for plasma jets working at atmospheric pressure. The only thing you can use is to inject small particles into your plasma jet and to try to follow their velocity by laser Doppler anemometry [11, 20-22]. But the results are not very good for two reasons. First, with very small particles you obtain

very scattered data because the scattered light is not very intense and the plasma light is very intense and you get a very low signal-to-noise ratio. Second, due to the Knudsen effect these particles will never follow the plasma gas velocity. Usually the best thing to do is to try to calculate a velocity distribution similar to that of the temperature distribution obtained from measurements of the gas enthalpy and the flow rate [9]. However, this distribution is not necessarily unique and some judgment has to be used. Then the velocity distribution is compared with the measured one to be sure that you have something that is reasonable.

If it is possible to measure small particle velocities in the plasma jet itself, then it is possible, of course, to measure the velocity of bigger particles and this can be achieved rather easily by laser anemometry with either counters or photon correlators to detect the signal [19,21-24]. The surface temperature of the particles can be measured by two-color photometry in flight [25]. But in that case, you have to be aware that in the plasma core itself the light emitted by the plasma is something like one or two orders-of-magnitude higher than the light emitted by the particles. This is due to the fact that in the plasma core, the temperature of the plasma is the highest and temperature of the particles is lowest; thus, the flux emitted from the particles, which to a first approximation is proportional to T^4, is rather low. Thus, the measurement of the surface temperature can be made only immediately after the plasma core for $T < 8000$ K at 1-atm), i.e., mainly in the plasma plume. No information can be obtained in the plasma core itself, except maybe information about the vaporization of the particles because the vapor cloud from the particles can be measured by absorption spectroscopy (using appropriate techniques with hollow cathodes to produce the emission of the corresponding metals). When you start, for example, with alumina particles, the pyrolysis of this vapor in the hot plasma surrounding the particles, soon yields the emission of aluminum spectra. If you use a hollow cathode of aluminum, you can measure the absorption of the aluminum present in the vapor and detect the evaporation rate of the particles after a few millimeters of their trajectory into the plasma jet. It's even possible when considering the emission from two lines of aluminum, to measure the excitation temperature of the vapor cloud around the particle, and then to find out if this excitation temperature is in equilibrium with the plasma temperature.

Once the model is developed and is compared with the measurements, the idea is to try to see how is it possible to determine the heat transfer coefficient and drag coefficient. This can be done by considering the drag equation, as well as the heat transfer equation. Knowing the velocity and temperature evolution of the particle along their trajectory mean values, we can from these equations determine the heat transfer coefficient, as well as the drag coefficient. These measurements will give only mean values and the precision of these mean values will be very poor as soon as you get into the regions where the velocity of the particles is on the order of the velocity of the plasma, because in these regions the precision of the calculations will be very poor. Once the heat transfer coefficient as well as the drag coefficient are known, we can try to relate them to the Nusselt number and to the Reynolds number, but then again we are back with the theories. The precision of these measurements may not allow us to determine which theory is the best, especially for the theories accounting for the steep variations of the temperature around the particle, as well as for the phenomenon we have neglected (e.g., the particle-charging effect, the particle-shape effect or the particle morphology).

References

1. E.Pfender, Pure and Appl. Chem., 57 (9), 1179 (1985).

2. J. A. Lewis, N. S. Gauvin, A.I.Ch.E., 19, 982 (1973).

3. X. Chen, E. Pfender, Plasma Chem. Plasma Proc., 3, 351 (1983).

4. E. Bourdin, Int. J. Heat Mass Transfer, 26, 567-582 (1983).

5. A. Vardelle, M. Vardelle, E. Bourdin, P. Fauchais, Proc. ISPC, 5, Heriot Watt University, Edinburgh, Scotland (1981).

6. T. Yoshida, Thesis, University of Tokyo (1976).

7. X. Chen and E. Pfender, "Heat transfer to a simple particle exposed to a thermal plasma," Plasma Chemistry and Plasma Processing, 2, 185 (1982).

8. X. Chen, H. P. Chyou, Y. C. Lee and E. Pfender, "Heat transfer to a particle under plasma conditions with vapor contamination from the particles," Plasma Chemistry and Plasma Processing, 5, 119 (1983).

9. A. Vardelle, M. Vardelle and P. Fauchais, Proc. ISPC 7, Eindhoven, 8-15 (1985).

10. Y. C. Lee and E. Pfender, "Particle dynamics and particle heat and mass transfer in thermal plasmas - Part III, Plasma Chem. Plasma Proc., to be published.

11. Y. P. Chyou, R. M. Young and E. Pfender, Proc. ISPC 7, Eindhoven, 15-17 (1985).

12. P. Fauchais, J. F. Coudert, A. Vardelle and J. Lesinki, "Diagnostics under thermal plasma conditions in plasma processing and synthesis of materials," Proc. Materials Research Society Annual Meeting, 30, Boston, MA, ed. Elsevier (1984).

13. P. Fauchais, K. Lapworth, J. M. Baronnet, "First report on measurement of temperature and concentration of excited species in optically thin plasmas," Report of the group for Standard and Measurements in Plasma Chemistry (April 1979), I.U.P.A.C. Subcommittee on Plasma Chemistry.

14. T. L. Eddy, J. Quant. Spectrosc. Radiat. Transfer, 3, 197 (1985).

15. J. F. Coudert, J. M. Baronnet and P. Fauchais, Proc. ISPC 6, Montreal, Paper A-4-2, ed. Prof. Boulos, University of Sherbrooke (1983).

16. K.Etemaldi and E. Pfender, Rev. Sci. Instruments, 53 (2), 12 (1982).

17. M. T. Mehmetoglu, F. Fitzinger and W. H. Gauvin, Rev. Sci. Instruments, 53 (2), 285 (1983).

18. D. Gravelle, M. Beaulieu, C. Carlor, D. Iaccoca and M. I.Boulos, Proc. ISPC 6, Montreal 1, 108, ed. Prof. Boulos, University of Sherbrooke (1983).

19. S. Cheng, M. Zimmerman and R. B. Miles, Appl. Phys. Lett., 43 (2), 143 (1983).

20. S. Fuji, M. Gomi and K. Eguchi, J. Fluids Eng., 105, 128 (1983).

21. F. Durst, A. Melling and J. H. Whitelaw, Principles and Practice of Laser Doppler Anemometry, Academic Press, New York (1976).

22. P. H. M. Vaessen, G. M. W. Kroesen and D. C. Schram, Proc. ISPC 6, Paper A-4-7, Montreal, ed., Prof. Boulos, University of Sherbrooke (1983).

23. A. Vardelle, M. Vardelle and F. Fauchais, Plasma Chem. Plasma Proc., 2, 255 (1982).

24. G. Gouesbest, Plasma Chem. Plasma Proc.., 5 (2), 91 (1985).

25. J. Mihsin, M. Vardelle, J. Lesinski, and P. Fanchais, Proc. ISPC 7, 724-729, Eindhaven, NL, July (1985).

26. A. V. Popov, Sixth International Symposium on Combustion, Newhaven, Connecticut (1956).

12.2 PLASMA-PARTICULATE INTERACTIONS: DENSE LOADING EFFECTS

MAHER I. BOULOS
Department of Chemical Engineering
University of Sherbrooke
Sherbrooke, Quebec, J1K 2R1

Introduction

Progress in the thermal treatment of powders under plasma conditions has been closely tied to our understanding of the basic phenomena involved in plasma-particle momentum and heat transfer. In this note, a brief discussion is presented of the principal achievements in this area over the last few years and present research needs.

Plasma-Particle Momentum and Heat Transfer

Considerable progress has been achieved in this area including:

- The development of correlations for plasma-particle heat and momentum transfer rates with appropriate corrections for the presence of steep temperature gradients. No universally-accepted correlation has, however, emerged. Substantial differences still exist between different relationships.

- Special attention has been given to the study of the following effects: Internal heat conduction in the particles; Effect of particle evaporation on the plasma-particle heat transfer rate; Knudsen effects for small particles; The effect of thermophoris and turbulent diffusion on particle trajectories in a plasma stream.

Plasma-Particle Interactions under Dense Loading Conditions

By far, most of the studies reported in literature has been limited to dilute flow situations in which the presence of the particles are assumed to have no effect on the plasma stream. It is becoming increasingly evident, however, that in a realistic situation the particle loading should be sufficiently high in order to make efficient use of the energy available in the plasma. The particle-source-in-cell [PSI-Cell] model has proven to be quite effective in this respect offering an appropriate means of accounting for plasma-particle interactions under dense loading conditions.

Areas Where a Specific Research Effort is Needed

- Systematic theoretical and experimental study of the plasma-particle momentum and heat transfer phenomena in an attempt to gradually converge on a limited number of universally accepted correlations for the calculation of the plasma-particle momentum and heat transfer rates. To a large extent, progress in this area will depend on the availability of appropriate diagnostic tools for the in-flight measurement of the principal particle parameters including the particle velocity, surface temperature and diameter.

- Further development of both theoretical and diagnostic tools for the study of plasma-particle interaction effects under dense loading conditions. Special attention is to be given to the effect of the presence of the particles on the characteristics of turbulent plasma flows which has hardly been explored.

THERMAL PLASMA RESEARCH AREAS

CHAPTER 13

NUCLEATION AND PARTICLE GROWTH

Session Chairman

M. Venugopalan
Department of Chemistry
Western Illinois University
Macomb, Illinois 61455

13.1 PARTICULATE NUCLEATION AND GROWTH IN PLASMA SYNTHESIS

S.L. GIRSHICK
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Depending on the material, on further processing steps and on the intended application, several properties of a plasma-produced powder are of interest. These include the powder composition, the mean particle size and size distribution, the crystal phase, and the nature and extent of agglomeration. Ultimately the control of these properties as a function of process operating parameters requires an understanding of the phenomena of particle nucleation and growth in a plasma reactor.

As we follow the synthesis process from the injection of reactants at the upstream end of the reactor to the formation of product at the downstream end, a simple model suggests the following sequence of events:

(1) The reactants are dissociated at the high temperatures ($T \sim 10^4$ K) prevailing in the plasma.

(2) Gas-phase recombination chemistry at temperatures less than about 5000 K forms the condensable vapor or precursor(s) of interest.

(3) As the plasma is quenched it becomes increasingly supersaturated with respect to this vapor, causing homogeneous nucleation to occur.

(4) Particles grow through collisions with each other and through condensation.

(5) Before being collected, the particles may become significantly agglomerated.

In modeling step 2 above, it is typical to assume that the species concentrations at each temperature are determined by the existence of chemical equilibrium; in fact the relevant chemical kinetic rates at these temperatures are rarely known. Given the high quench rates ($\sim 10^6$ K/s) typical of a plasma reactor, important reaction steps may in fact not be in equilibrium.

Several detailed models have been developed for estimating nucleation and growth rates. These include classical nucleation theory, which assumes a stationary, nonreacting system and is based on the energy barrier represented by a particle's free surface energy [1-2]; the computer codes developed by Gelbard and Seinfeld, in which the time-dependent dynamical balance equation is solved for particles of all size classes in a nonreacting system [3]; the particle "clearance volume" concept advanced by Alam and Flagan [4]; and the "zero activation energy" model proposed by McMurry, in which Gelbard's and Seinfeld's work was extended to reacting systems [5].

Beyond the simplest models or the general nucleation and growth models available, several factors which are peculiar to plasma reactors may have important effects on nucleation and growth. These include the role of heterogeneous reactions on the surface of formed particles, the influence of seed particles on nucleation rates [4], the choice of main plasma gas (noble vs.

molecular), incomplete mixing of injected reactants, quench rates, and particle residence times.

Several directions are indicated for research in this area. The zero-activation approach appears to be the most promising for modeling the rapid-quench plasma reactor environment, assuming that it can be modified to account for inhomogeneous reaction rates. Limitations exist with respect to the data base for chemical kinetics, both in the gas phase and at the surface, and in the effect of charged particles on nucleation rates.

A variety of experimental techniques can be employed to support the modeling. These include off line examination of collected powders, on line particle sampling, and in situ optical diagnostics. Ideally the latter might include spatially-resolved measurements of temperature, velocity and particle size. A number of studies in the area of soot particle nucleation and growth in flames may provide some guidance in the application of light-scattering techniques to plasma reactor conditions. The ultrafine particles of interest are typically in the Rayleigh regime for optical scattering, for which either static (e.g., the "scatter-extinction" method [6]) or dynamic (diffusion-broadening spectroscopy) techniques, or a combination of the two [7], have been used to determine mean particle size and number density in sooting flames.

References

1. Becker, R. and Döring, W., Ann. d. Phys. 24, 719-752 (1935).

2. Lothe, J. and Pound, G.M., J. Chem. Phys. 36, 2080-2085 (1962).

3. Gelbard, F. and Seinfeld, J.H., "Simulation of multicomponent aerosol dynamics," J. Colloid Interface Sci. 78, 485-501 (1980).

4. Alam, M.K. and Flagan, R.C., "Simultaneous homogeneous nucleation and aerosol growth," J. Colloid & Interface Sci. 97, 232-246 (1984).

5. McMurry, P.H., "New particle formation in the presence of aerosol: rates, time scales, and sub-0.01 μm size distributions," J. Colloid Interface Sci. 95, 72-80 (1983).

6. D'Alessio, A., "Laser light scattering and fluorescence diagnostics of rich flames produced by gaseous and liquid fuels," pp. 207-256 in Particulate carbon: formation during combustion, edited by D.C. Siegla and G.W. Smith, New York, Plenum, 1981.

7. Flower, W. L., "Optical measurements of soot formation in premixed flames," Combust. Sci. & Tech. 33, 17-33 (1983).

Blank Page

THERMAL PLASMA RESEARCH AREAS

CHAPTER 14

INFERENCES DRAWN FROM RECENT STUDIES ON THE ROLE OF PLASMA TECHNOLOGY

J. V. R. Heberlein
Westinghouse R & D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

14. INFERENCES DRAWN FROM RECENT STUDIES ON THE ROLE OF PLASMA TECHNOLOGY

J. V. R. HEBERLEIN
Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

Over the past ten years, there has been a proliferation of studies and workshops dealing with the importance of plasma technology for a variety of applications. Eight of these studies (see Table I) performed since 1980 have been selected and reviewed in this section. The review neglects the portions of the studies dealing with low pressure plasmas because of the emphasis on thermal plasmas in the present workshop. I first will summarize the approach and the results of each study, then I will comment on the parallels and discrepancies of approaches and results, and finally, conclusions obtained from the comparison of these studies and the present workshop will be presented.

14.1 Summary of the Studies

1. NSF Workshop on Plasma Chemistry and Arc Technology, Minneapolis, MN, 1980.

Approach: A number of experts provided short overviews of a wide variety of subjects in both thermal plasma and low pressure plasma areas. The proceedings contain more detailed contributions from the participants.

Results:

(a) The driving potentials for bringing plasma technology to industrial application were identified to be:

- The critical status of the supply of strategic materials, which can be alleviated by the use of plasma technology for recycling, material conservation (e.g., by plasma spraying), and for the generation of new materials with comparable or improved properties (plasma synthesis).
- Increasing environmental restrictions for chemical processing of materials promotes plasma processing as an attractive alternative (as long as electricity is produced without pollution).
- Low capital investment is required because of the smaller size of plasma installations for comparable production rates.
- Plasma spraying and plasma materials synthesis has little competition from other technologies.
- A decreasing electricity to oil cost ratio will make plasma processes economically more competitive.

(b) The major industrial developments at that time were (the present state is given in parenthesis):

- Blast furnace firing (still being developed in France).
- Direct reduction reformers (only used in Sweden).
- Ferroalloy reduction and plasma smelting (partially commercialized, partially under development).

- Reactive metal/solar grade silicon generation (development suspended).
- Coal pyrolysis, desulfurization (only development work in Germany and Eastern Europe for acetylene production).
- Cement production and N_2 fixation.

(c) Major large scale developments were recommended:

- Reclamation of valuable scrap materials.
- Near net-shape manufacturing using plasma spraying.
- Secondary materials recovery from slags.
- Concentration of trace elements.
- Generation of "new" materials, e.g. high-temperature ceramics or alloys.

Table I - List of Plasma Technology Surveys

1. NSF Workshop on Plasma Chemistry and Arc Technology, Minneapolis, Minnesota, 1980; Proceedings edited by H. J. Oskam and E. Pfender.

2. Plasma Technology and its Industrial Applications, G. K. Bhat, 1981, survey report funded by EPRI.

3. Plasma Processing or Materials Production, Westinghouse (M. Down), 1982, funded by EPRI.

4. A Review of the Applications of High-Temperature Plasma Arcs in Thermal Processing, K. Tennankore, AEC, Ltd., 1984, Canada.

5. Plasma Technology: Review of the State of the Art and its Potential in Canada, IREQ (M. R. Drouet), 1984, Canada, funded by the Canadian Electric Association.

6. Plasma Processing of Materials, National Materials Advisory Board, National Research Council, 1985.

7. New Developments in Plasma Technology, Business Communications Co., Inc., (E. Lerner), 1985.

8. Potential of Plasma Technology, G. Ecker, et. al., VDI - Verlag, Germany, 1985 (in German).

(d) The research needs identified in this study were:

- Fundamental process understanding for optimization.
- Plasma-particle, plasma-melt interaction, in particular heat, mass, and momentum transfer and intermediate reactions including gas adsorption or desorption.
- Catalytic effects generated by the presence of a plasma, such as the influence of charged or metastable particles.
- Development of diagnostics for use with practical systems for providing direct feedback for process optimization and control.
- Investigation of electrode effects.
- Determination of thermodynamic and transport properties.
- Models for process kinetics, including heterogeneous reactions, and powder product formation, possibly leading to scaling laws.
- Both interdisciplinary approaches and university-industry cooperation were strongly recommended.

2. *Plasma Technology and Its Industrial Applications, G. K.Bhat, 1981, funded by EPRI*

Approach: Personal evaluation of a number of specific sites where industrial developments in plasma technology were pursued.

Results:

(a) The technological initiative for plasma developments was found to have moved from the U.S. to Japan, the USSR and East Germany.

(b) It is recommended to select specific processes which appear to be particularly promising applications of plasma technology and obtain funding for process development through the pilot-plant verification stage, and for supporting research.

3. *Plasma Processing for Materials Production, Westinghouse, (M. Down), 1982), funded by EPRI.*

Approach: Technical and economic analysis of selected applications of plasma technology utilizing experts in different fields.

Results:

(a) Technical feasibility was demonstrated for several processes,but there is a definite need for scaling processes from the laboratory experiments to the pilot plant stage to uncover practical problems related to the scale-up, and to obtain more detailed information on the economics of the process.

(b) The most promising process identified for scale-up was the iron-chip melting in a plasma-fired shaft furnace.

(c) The specific R&D topics which would have the most significant impact on establishing an integrated plasma process were thought to be the injection of coal powder into a plasma, and the collection of particulates from a plasma.

4. Applications of High-Temperature Plasma Arcs in Thermal Plasmas, Tennankore, AEC, Canada.

Approach: A limited literature study and discussion with experts led to recommendations on the use of available capabilities in the nuclear research and development institutes for the enhancement of plasma technology for industrial applications.

Results:

(a) Capabilities exist within the nuclear establishment to study optimum electrode cooling and gas quenching.

(b) Investigations which will have benefits to nuclear technology as well are plasma-jet ignition and the generation of aerosols using plasmas.

(c) The production of synfuel using plasma technology was seen as a long-term development worth pursuing.

5. Plasma Technology: Review of the State of the Art and Its Potential in Canada, IREQ (Drouet), 1984, funded by the Canadian Electric Association.

Approach: In this study, a large number of managers in industry were interviewed directly via a questionnaire with regard to their view of plasma processes. The study was specific for Canada and was aimed at obtaining data for future electricity consumption.

Results:

(a) Industry sees the advantage of plasma processes in increased operating flexibility and improved process control. However, only when these advantages are coupled with an adequate return on the investment and with capital savings, will plasma processes be accepted. Few see operating cost benefits through the introduction of plasma processes, but the possibility of capital cost savings is generally acknowledged.

(b) In the views of industry, the reliability of the plasma equipment is not yet proven. Full scale process demonstration is required for acceptance. These developmental efforts should be subsidized to reduce the risk.

(c) The most promising applications for plasma technology were seen as blast furnace air preheating, reformer gas generation, and drying.

(d) Recommendations were:

- Evaluation of long-term, plasma-heater operation, in particular electrode-life studies.
- Pilot-scale process studies.

6. Plasma Processing of Materials, National Materials Advisory Board, NRC, 1985.

Approach: A committee of renowned scientists and technological leaders prepared a detailed report on the status and future of plasma technology for several applications related to materials processing. The majority

of the participants was connected to some activity in the plasma field.

Results:

(a) It was found that the technological innovation in the plasma area has moved from the U.S. to the USSR, Japan and East Germany.

(b) In the U.S., the principal driving potential for utilizing plasma technology was seen as improved utilization of strategic materials, near net-shape processing, and generation of novel refractory powders.

(c) The specific applications with particular promise were seen to be:

- Remelting for materials recycling.
- Extractive metallurgy.
- Rapid solidification of prealloyed powders, of amorphous or metastable films, and for near net-shape manufacturing.
- Synthesis of novel ceramics.

(d) Recommendations for research are:

- Studies of the basic process kinetics.
- Improvement of the diagnostic capabilities for process monitoring.
- Determination of transport properties.
- Modeling of the plasma-materials interface.

7. New Developments In Plasma Technology, Business Communications Co., Inc., 1985.

Approach: Information from a variety of sources was used to predict market growth for several plasma applications. The state of the technology was deduced from information from experts involved in plasma related work and from the patent literature. For the market predictions, the usual extrapolations from statistical data were made. A constant electricity to oil cost ratio was assumed.

Results:

(a) Thermal plasma technology is anticipated to grow in industrial importance because of a few specific applications with large growth potential.

(b) Waste pyrolysis is the application with the largest potential for growth. It is seen as a $3.8 billion market in 1995. The main reason for this conclusion is the compactness of the plasma installation and the uncertain technical status of competitive technologies.

(c) Plasma cutting and plasma metallurgy are seen as growth markets with limited potential because (a) these applications are strongly tied to the status of the steel industry, and (b) their economic potential is dependent on the electricity cost.

8. Potential of Plasma Technology, G. Ecker, et. al., VDI – Verlag, Germany, 1985.

Approach: Six plasma applications were evaluated according to the impact they have with regard to six criteria.

The applications were:

(a) Welding, cutting, and melting.
(b) Circuit interruption.
(c) Lamps.
(d) Thermal plasma processing.
(e) Low-pressure plasma processing.
(f) Pulsed power.

The evaluation criteria were:

(a) Product quality improvement.
(b) Social relevance.
(c) Economic impact.
(d) Environmental impact.
(e) Humanization of the work environment.
(f) Conservation of raw materials.

Information was gathered using the Delphi method, through interviews with a large number of experts.

Results:

(a) Plasma spraying was seen as having a good growth potential because there are no competing technologies for:

- Near net-shape manufacturing.
- Multiple layer coatings.
- Underwater coatings.
- High-temperature coatings.

(b) Of similarly high-technological interest was plasma synthesis of new materials, in particular high-temperature ceramics and pigments.

(c) The attractions of plasma technology to metallurgical applications are seen as:

- Materials conservation and scrap reclamation.
- Reduced environmental contamination and noise pollution.
- Ease of process automation.

(d) Competitive processes for plasma welding and cutting are in their infancy. Plasma processes are of particular interest to underwater welding and cutting which is gaining in importance.

(e) Thermal plasma processing has found limited acceptance in spite of technological advantages because (a) the economics is often strongly dependent on electricity cost, and (b) hostility towards change to "high technology" in traditional industries is still widespread. Development

should concentrate on high value-added processes, processes where a significant environmental impact can be achieved, and on geographical locations with inexpensive electricity.

Technology R&D needs:

(a) The major issues are:

- Need for high-power plasma generators (100MW).
- Control of material injection into the plasma and product collection from the plasma.
- Improved efficiency through improvements in heat recovery.
- Underwater operation of plasma torches for spraying, cutting and welding.

(b) Detailed understanding of the specific processes would be required to take full advantage of the plasma process potential for automation. This is particularly difficult because optimization requires variation of many parameters.

(c) The status of plasma technology in industry would be advanced through basic research in:

- Electrode phenomena.
- Plasma-material interaction.
- Development of diagnostics for practical systems.
- Nonequilibrium effects due to large gradients, and charged particle effects on reaction kinetics.
- Discharge modeling, in particular the discharge stability criteria.

(d) Applications-oriented research should be conducted, in particular diagnostics on practical plasmas leading to process understanding for automation.

(e) Research should be conducted in interdisciplinary groups, and cooperation between universities and industries should be encouraged.

(f) A strong marketing effort should be undertaken to improve acceptance of plasma technology.

14.2 Comparison of Methods and Results

Several observations are very distinct:

1. The majority of the studies was performed by scientists with a certain affinity for plasma technology, using input from a variety of technological experts in plasmas. The consequence was (a) the technological evaluations were very competent and thorough, and (b) because there exists only a limited pool of experts in plasma technology, these experts contributed to several of these studies, resulting inevitably in a similarity of the conclusions.

2. The study performed by IREQ stands out insofar as strong input from business executives is reported who view plasma technology only as one of several means to an end.

3. In almost all studies, discussion of developments in rival technologies is neglected. Parts of the NMAB report are exceptions. This is an important shortcoming and it can influence the validity of the conclusions.

4. The majority of the studies assumed that the cost of electricity will decrease compared to the cost of oil, continuing a trend prevalent in the seventies. This decrease has not continued in the eighties and it is doubtful that it will resume in the foreseeable future.

5. All studies see major opportunities for steady implementation of plasma technology where well identifiable technological advantages which will economically offset the disadvantage of using an expensive form of energy.

6. Recommendations for research approaches are strikingly unchanged over the five-year period, in particular, the pleading for larger scale developments with associated research.

7. Some of the recommendations from earlier studies have been successfully implemented, both with regard to larger scale projects (e.g. the chip melting cupola) and with regard to basic-research project selection.

14.3 Conclusions

A critical evaluation of the studies results in these conclusions:

1. The major driving forces for bringing plasma technology into industrial utilization (i.e. resulting in economic benefits) are:

   - Environmental considerations both on the front end and on the back end of the process. Examples are, the avoidance of environmental hazards through the use of plasma technology in the manufacturing of a product without a hazardous by-product, and the use of plasmas for destroying environmentally hazardous by-products.

   - The potential for process automation and process path simplification.

   - Comparable throughput with smaller installations resulting in capital cost savings.

   - Scarcity of some materials requiring recovery processes and/or reduced consumption by different processes (i.e., coatings or near net-shape manufacturing), or the generation of new materials.

2. Metallurgical processing has a special fascination because it is the largest volume application. However, the market has been depressed, and incentives for major investments are expected to exist only in certain geographical areas with low electricity cost. The strong efforts in this area reported in this workshop gain therefore particular weight, because they are industrial developments on their way to commercialization.

3. Plasma waste destruction and ceramic powder generation appear as applications of high potential because of the high value added in the process and because of the large anticipated growth of the market.

4. There continues to be a need for large-scale process-verification experiments for demonstration of the advantages of the plasma process and for identification of further research and development needs. Shared funding of such projects may make the risk of failure acceptable.

5. There continues to be a need for basic research in:

   - Diagnostics on practical plasmas.
   - Modeling of and property calculations for practical systems, resulting in process optimization and scaling relations.
   - The interactions between different components of a plasma-process system, e.g., reactant injection into a plasma or product collection from a plasma.
   - The interactions between the plasma and solid/liquid surfaces, e.g., plasma-melt, plasma-particulate, plasma-electrode, etc.
   - Electrode-life studies.

6. Interdisciplinary research and industry-university cooperation are generally seen as beneficial for any development of plasma technology for an industrial application.

7. The strong industrial development efforts presently underway in specific thermal plasma applications are probably the strongest testimony for the usefulness and the continued growth of this technology in industry. One has to realize that this continued growth will probably be due to relatively select applications.

8. The present workshop (which focuses on the thermal aspects of select plasma processing applications) amplifies several of the conclusions of the previous studies and provides more detail in some of the discussions. There is essentially no discrepancy in the results. Future studies and workshops may benefit from emphasizing the systems considerations, which might also include discussions of the technological challenges, for example, of product collection or separation in conjunction with a plasma process or of diagnostics of the plasma-melt interface region.